AUTOXIDATION INHIBITION IN TETRALIN

By

NICHOLAS MICHAELS

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA
June, 1961

ACKNOWLEDGMENTS

The writer wishes to express his sincere appreciation to Dr. W. T. Lippincott for his friendship, inspiration and excellent direction of this research.

The writer would also like to sincerely thank his wife, Linda, for her moral support and assistance in the preparation of the manuscript.

TABLE OF CONTENTS

Page

ACKNOWLEDGMENTS ii

LIST OF TABLES v

LIST OF FIGURES vi

INTRODUCTION 1

- I. Aims and Scope 1
- II. Autoxidation 2
- III. Induction Period and Inhibition 11
- IV. Cobalt Ions in Autoxidation Systems 15

EXPERIMENTAL 17

- I. General 17
- II. Purification of Tetralin 18
- III. Other Chemicals 21
- IV. Apparatus 25
- V. Sample Preparation 28
- VI. Interpretation of a Typical Autoxidation Run 30

RESULTS 33

- I. The System 2, 2'-Azobisisobutyronitrile and Inhibitor in Tetralin 34
- II. The System Cobalt (II) Naphthenate, Tetralin Hydroperoxide and Inhibitors in Tetralin 51

TABLE OF CONTENTS (Continued)

Page

III. Cobalt (II) Naphthenate and 2, 2'-Azobisisobutyronitrile with Other Additives 64

DISCUSSION 80

I. The Inhibition Process in Non-Branching Initiator Systems 81

II. The Inhibition Process in Branching Catalyst Systems 88

III. Kinetics of Cobalt (II) Naphthenate Catalyzed Autoxidation of Tetralin 95

SUMMARY 99

BIBLIOGRAPHY 101

APPENDIX 105

BIOGRAPHICAL SKETCH 109

LIST OF TABLES

		Page
1.	Temperature Calibration of Bath	27
2.	Data for a Typical Autoxidation Run	31
3.	Effect of Hydroquinone on Induction Period at 60°	37
4.	Effect of Hydroquinone on Induction Period at 70°	39
5.	Effect of Hydroquinone on Induction Period at 80°	41
6.	Effect of Dibutylcresol on Induction Period at 60°	44
7.	Effect of Dibutylcresol on Induction Period at 70°	46
8.	Effect of Dibutylcresol on Induction Period at 80°	47
9.	Apparent Stoichiometry from Runs with Short Induction Periods	49
10.	Effect of Hydroquinone on Induction Period	52
11.	Effect of Hydroquinone on Induction Period	55
12.	Effect of Dibutylcresol on Induction Period	57
13.	Effect of Dibutylcresol on Induction Period	59
14.	Effect of Tetralin Hydroperoxide on Induction Period	61
15.	Effect of Cobalt (II) Naphthenate on Rate of Oxygen Uptake	65
16.	Effect of Water on Cobalt Systems	68
17.	Effect of Quinone on Cobalt Systems	70
18.	Effect of Tetralin Hydroperoxide on Cobalt Systems	73
19.	Effect of *p*-Methoxyphenol Concentration on Induction Period	78

LIST OF FIGURES

Page

1. Plot of Oxygen Pressure versus Time for a Typical Autoxidation Run 32
2. Plot of ΣR versus $[HQ]_o$ at 60^o 38
3. Plot of ΣR versus $[HQ]_o$ at 70^o 40
4. Plot of ΣR versus $[HQ]_o$ at 80^o 42
5. Plot of ΣR versus $[DBC]_o$ at 60^o 45
6. Plot of t_i versus $[HQ]_o^3$ 53
7. Plot of ln t_i versus $[HQ]_o$ 56
8. Plot of ln t_i versus ln $[DBC]_o$ 58
9. Plot of t_i versus ln $([THP]_o - [DBC]_o)$ 60
10. Plot of t_i versus ln$[THP]_o$ 62
11. Plot of ln Rate versus ln$[Co]_o$ 66
12. Plot of ln Rate versus ln$[H_2 0]_o$ 69
13. Plot of ln Rate versus ln$[Quinone]_o$ 71
14. Plot of Rate versus $[THP]_o$ 74
15. Plot of t_i versus ln $(2 \alpha [AIBN]_o - S[HQ]_o)$ 83
16. Plot of t_i versus ln $(2 \alpha [AIBN]_o - S[DBC]_o)$ 84
17. Plot of t_i versus $1/[THP]_o$ 93
18. Plot of t_i versus $1/[Co]_o^3$ 94

INTRODUCTION

I. Aims and Scope

The aim of this study is to investigate the inhibition processes that occur during the induction period in tetralin autoxidations. The experimental approach to this problem is divided into three main sections.

The first section is a study of a system containing tetralin substrate, the initiator 2, 2'-azobisisobutyronitrile and the phenolic inhibitors dibutylcresol and hydroquinone. Quantitative information about the processes occurring during the induction period was used to determine the stoichiometry of the inhibitors employed and the radical-producing efficiency of the initiator.

The second section is concerned with the system tetralin, cobalt (II) naphthenate, tetralin hydroperoxide and the same phenolic inhibitors used in the first section. This system was studied to determine the effect of the branching reaction on the inhibition process.

The last section is an investigation of the effects of various additives 2, 2'-azobisisobutyronitrite and cobalt (II) naphthenate systems. These systems were studied in order to clarify some of the aspects of the mechanism of branching catalysts.

The experimental procedure used was to vary the concentration and temperature parameters and measure the effect produced in the system. The effects were measured by changes in the induction period or by the rate of oxygen absorption.

II. Autoxidation

Autoxidation is the term used to describe reactions between organic compounds and molecular oxygen that occur at relatively low temperatures and in the absence of a flame or spark. The scope of these reactions is vast, ranging from metabolism to deterioration of lubricating oils.

The majority of autoxidation reactions proceed by a free radical chain process and indeed, the paramagnetic oxygen molecule can itself be considered a diradical. Bäckström (1) in 1927 showed that the photochemical reaction of aldehydes and oxygen was markedly retarded by the addition of small amounts of an inhibitor and that the reaction gave quantum yields of 10,000 to 15,000 which he attributed to a radical chain process. A host of workers (2, 3, 4, 5, 6) since then have shown that autoxidations are inhibited by traces of antioxidants and catalyzed by metal salts such as those containing cobalt, manganese, iron, lead and copper.

The generally accepted mechanism (5, 6, 7, 8) for free radical liquid-phase autoxidations is as follows. The initiation step can be represented as:

$$RH + \text{initiator} \longrightarrow R\cdot \qquad (1)$$

The propagation reactions are:

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (2)$$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \qquad (3)$$

Termination in the absence of added inhibitor can be any of the three possible combinations:

$$2\ ROO\cdot \longrightarrow \text{products} \tag{4}$$

$$2\ R\cdot \longrightarrow \text{products} \tag{5}$$

$$ROO\cdot + R\cdot \longrightarrow \text{products} \tag{6}$$

In the presence of an inhibitor, the termination step may be generalized by:

$$ROO\cdot + A \longrightarrow \text{products} \tag{7}$$

In the above equations RH is the substrate, $R\cdot$ is the substrate radical, $ROO\cdot$ is the peroxy radical, ROOH is the hydroperoxide and A is the inhibitor (antioxidant). Each of these steps will now be considered in more detail.

A. Initiation

Initiation of autoxidation may be effected by heat, light, radiation, transition metal ions (9-12) and free radical sources such as azo compounds or peroxides (7, 13, 14).

Verdin (15) recently reported his investigation on the autoxidation of tetralin induced by Co^{60} γ-radiation. He found that the reaction proceeded by a chain mechanism and that the principal termination reaction in the absence of inhibitor is by interaction of two peroxy radicals.

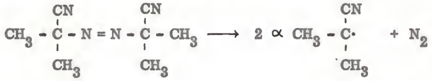
Metal ions which initiate autoxidation are generally those having two or more oxidation states with a suitable oxidation-reduction potential. Examples are cobalt, copper, manganese and iron. There have been a number of theories proposed to explain the role of metal ions in autoxidation reactions. Briefly, the two main theories are:

1. that the metal reacts with hydroperoxide in the system to produce radicals which can initiate additional chains;

2. that the metal acts as an oxygen carrier which then reacts with the substrate to produce radicals.

These and other theories will be discussed in Part IV of this section.

Compounds that have a covalent bond with a dissociation energy of 20-40 kcal. provide a convenient source of free radicals. For practical use in kinetic studies, the radicals would be produced at a predictable rate and be sufficiently reactive. Azo compounds generally follow these conditions and 2, 2'-azobisisobutyronitrile (AIBN) has been used by a number of investigators (7, 13, 14, 16) as a convenient source of free radicals. AIBN decomposes by strictly first-order kinetics at a known rate (17) which is essentially independent of the solvent (16, 18). It does not undergo induced decomposition by radicals or oxygen (19, 20). The decomposition to free radicals occurs as follows:



$$CH_3 - \underset{CH_3}{\overset{CN}{C}} - N = N - \underset{CH_3}{\overset{CN}{C}} - CH_3 \longrightarrow 2\ \alpha\ CH_3 - \underset{CH_3}{\overset{CN}{C\cdot}} + N_2 \qquad (8)$$

where α is the efficiency of radical production. The significance of α will be explained in the Results section. Hammond et al. (20) have recently published the results of an extensive study of the decomposition of AIBN. The 2-cyanopropyl radical resulting from AIBN decomposition can couple to give tetramethylsuccinonitrile or rearrange and couple to give the unstable (21) dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR'). The yields are dependent on solvent and conditions. In the presence of an antioxidant, the formation of RR' decreases and none is formed in carbon tetrachloride in the presence of oxygen at 62.5°.

B. Propagation

The propagation reactions:

$$R\cdot + 0_2 \xrightarrow{k_a} R00\cdot \qquad (9)$$

$$R00\cdot + RH \xrightarrow{k_b} R\cdot + R00H \qquad (10)$$

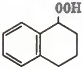
produce a hydroperoxide molecule and regenerate a substrate radical. In this sequence, reaction 9 is generally much faster than reaction 10. For tetralin at 25° the values for k_a and k_b are reported (22) to be 67.6×10^6 and 13.3 sec.^{-1} respectively. Repetition of the propagation process constitutes the chain reaction that causes the high quantum yields.

The rate of reaction 10, the rate determining step, is dependent on a number of factors such as the resonance stability of the radical formed ($R\cdot$) and the electron availability at the C - H bond (23). In general, electron donating groups increase the rate of reaction and electron withdrawing groups decrease the rate. This has been interpreted to be due to resonance in the transition state. The following mechanism:

$$R00\cdot + R'H \rightarrow \underset{\text{I}}{[R00:^{-}\ H^{+}\cdot R']} \leftrightarrow \underset{\text{II}}{[R00{:}H\cdot R']} \rightarrow R00H + R'\cdot \qquad (11)$$

proposed by Russell (23) shows that structure I will be stabilized by electron donating groups in R' and structure II shows the effect of stability of the incipient radical upon the reactivity of the C - H bond.

Some hydroperoxides such as those of tetralin, cumene and decalin are stable (3, 4, 24) and can be isolated in good yield. Tetralin hydroperoxide has been shown to be stable at 70° in uncatalyzed tetralin autoxidation systems (25). It was first isolated by Hartman and Seiberth (26) who proved it has structure III.



III

(12)

The isolation procedure used was fractional distillation at low temperatures and pressures. A second method is cold aqueous extraction followed by cold neutralization (27).

The decomposition of hydroperoxides can follow any of four main paths: spontaneous homolytic decomposition, metal ion catalyzed homolytic decomposition, acid catalyzed heterolytic decomposition and base catalyzed heterolytic decomposition (3, 4, 6). The first two processes are of importance in this work.

The uncatalyzed homolytic decomposition of secondary hydroperoxides is rather complex and leads to a variety of products. Vaughan et al (28) have summarized the more important reactions as follows:

$$R'_2CHOOH \longrightarrow R'_2CHO\cdot \ + \ \cdot OH \qquad (13)$$

$$R'_2CHO \xrightarrow{RH} R'_2CHOH \ + \ R\cdot \qquad (14)$$

$$R'_2CHO \xrightarrow{R\cdot} R'_2CO \ + \ RH \qquad (15)$$

$$R'_2CHO \xrightarrow{RO\cdot} R'_2CO \ + \ ROH \qquad (16)$$

The principal decomposition products of tetralin hydroperoxide (THP) are 1-tetralone, water and some 1-tetralol. Minor products reported include γ-o-hydroxyphenylbutyric acid and the corresponding aldehyde, dihydronaphthalene and oxygen (11, 29, 30, 31).

The kinetics of hydroperoxide decomposition is rather complex as would be expected. Medvedev (32) derived a two-term expression for the autoxidation of tetralin:

$$\frac{-d\,[RH]}{dt} = \frac{A\ [RH]^2}{1 + C\,[O_2]} + B[RH]\,[THP] \qquad (17)$$

where A, B and C are combinations of rate constants. During the initial stages of the autoxidation when the THP concentration is very low, the reaction is zero-order in THP. After the reaction has proceeded for a while, the second term becomes important and the hydroperoxide dependency becomes first-order. Robertson and Waters (33) studied the decomposition of pure THP and found that the first-order kinetics rate law was followed. This indicated that the homolytic decomposition resulted in alkoxy and hydroxy radicals. However, studies of the solvent effects indicated that the radicals formed reacted with the solvent to initiate chain reactions which could also decompose the hydroperoxide. At high THP concentrations the following chain mechanism assumed importance:

$$\cdot OH + R_2CHOOH \longrightarrow H_2O + R_2\dot{C}OOH \qquad (18)$$

$$R_2\dot{C}OOH \longrightarrow R_2C{=}O + \cdot OH \qquad (19)$$

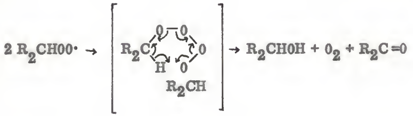
Experimentally it was found that THP decomposition followed first-order kinetics below 0.12 grams per ml. but that higher concentrations caused the decomposition to become more rapid. The decomposition of other hydroperoxides have also been shown to be complex. Bateman (6) found that olefin hydroperoxides decompose by first-order kinetics at concentrations below 10^{-2} M and at low temperatures. At higher concentrations the hydroperoxide dependency becomes second-order which he attributed to hydrogen bonding as follows:

$$\begin{tikzcd} 2\,\mathrm{ROOH} \arrow[r, shift left] \arrow[d, "\text{1st. order}"] & \overset{\mathrm{H}}{\mathrm{ROO}\cdots\mathrm{HOOR}} \arrow[l, shift left] \arrow[d, "\text{2nd. order}"] \\ 2\,(\mathrm{RO}\cdot + \cdot\mathrm{OH}) & \mathrm{RO}\cdot + \mathrm{H_2O} + \mathrm{ROO}\cdot \end{tikzcd} \qquad (20)$$

In summary, the decomposition of tetralin hydroperoxide is complicated by a number of factors including concentration, solvent, temperature and induced decomposition.

C. Termination

The termination reaction in the absence of added inhibitors or catalysts has been investigated by a number of workers. Russell (34) has proposed that for primary and secondary peroxides the termination step is:



(21)

He based this mechanism on the results of the following studies using deuterated compounds:

$$2\ R_2CHOO\cdot \xrightarrow{k_h} R_2C{=}O + R_2CHOH + O_2 \tag{22}$$

$$2\ R_2CDOO\cdot \xrightarrow{k_d} R_2C{=}O + R_2CDOD + O_2 \tag{23}$$

The reaction rate of the undeuterated compound was twice that of the deuterated one ($k_h/k_d = 2$). Woodward and Mesrobian (12) in their investigation of tetralin autoxidations proposed the following mechanism to account for the observed products:

$$2\ R_2CHOO\cdot \longrightarrow O_2 + 2\ [R_2CHO\cdot] \longrightarrow R_2C{=}O + R_2CHOH + O_2 \tag{24}$$

where the alkoxy radical is short lived and interacts rapidly to yield the products shown.

A number of other investigators (4, 7, 9, 35) have agreed that the most important termination process involves the two peroxy radicals since the rate of the reaction is independent of oxygen pressure above 100 mm. of mercury and the peroxy radicals are present in the highest concentration.

Robertson and Waters (36) considered the main termination reactions in branching uninhibited autoxidations to be:

$$ROO\cdot + \cdot OH \longrightarrow ROH + O_2 \tag{25}$$

$$R\cdot + \cdot OH \longrightarrow ROH \tag{26}$$

where ROH is tetralol. Under special conditions such as low oxygen pressure, termination steps 5 and 6 may become important (37).

In summary, the autoxidation of tetralin has been studied by a number of investigators. The basic mechanism of the reaction has been fairly well established and a number of theories have been proposed to account for the observed products. It is apparent that the results obtained can vary considerably depending on the system studied. The following sections will deal with the inhibitors and catalyst used in this research.

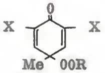
III. Induction Period and Inhibition

Free radical autoxidations are characterized by an initial period of time during which no observable oxygen uptake occurs. This interval is known as the induction period. The end of the induction period is signaled by a rapid oxygen uptake which is caused by the propagation steps becoming important.

Some early investigators (38, 39, 40) found that induction periods were not reproducible but, as was inferred in the previous section, the induction period is very sensitive to trace impurities such as peroxides, metal ions and adventitious inhibitors. Careful experimental procedures, purification and storage have led to reproducible induction periods which have now become a useful method for studying autoxidation reactions (7, 34, 35, 41).

The effect of an inhibitor on the induction period has been studied by a number of workers. Sacrificial inhibitors such as phenols and aromatic amines apparently prevent the propagation step by reacting with the chain propagating radicals (42).

Campbell and Coppinger (42) studied the reaction of dibutylcresol (DBC) and t-butyl peroxide in t-butanol. They isolated product (IV) and proved its structure.



IV (27)

where X represents the t-butyl group. To account for this, they postulated the following mechanism:

$$Ar0H + R\cdot \longrightarrow Ar0\cdot + RH \tag{28}$$

$$Ar0\cdot + R00\cdot \longrightarrow IV \tag{29}$$

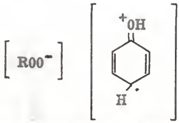
where Ar0H is DBC, R· is the substrate radical and the other symbols have their usual significance. In tetralin substrate, under one atmosphere of oxygen, the first step would probably involve R00· instead of R· as was explained in the previous section. The radical Ar0· is resonance stabilized so no new chains are formed, but it is an antioxidant and reacts with R00· in the second step. Russell (5) postulated a similar sequence of reactions differing in that R00· radicals were the attacking species and that the first step was addition to the ring and the second was hydrogen abstraction. Bickell and Kooyman (43) have also isolated compounds similar to structure IV and reported that termination involves two peroxy radicals since the concentration of R· is low due to its rapid reaction with oxygen.

Hammond et al.(44-47) in a series of papers proposed that the inhibition by weak antioxidants such as aromatic amines and phenols does not proceed by a discrete step involving hydrogen abstraction. Instead the antioxidant (A) functions by forming a charge-transfer complex with a peroxy radical which can then react with a second peroxy radical.

$$ROO\cdot + A \longrightarrow [A \rightarrow ROO\cdot] \qquad (30)$$

$$[A \rightarrow ROO\cdot] + ROO\cdot \longrightarrow \text{products} \qquad (31)$$

Walling (3) suggested that in the case of phenol, this complex might be represented as:



(32)

The main reason for Hammond's proposed mechanism was that no kinetic isotope effect was noted in the reaction where N-D-diphenylamine or N-D-N-methylaniline was compared to the undeuterated amine. He also found that dimethylaniline was a weak inhibitor and that N, N'-tetramethyl-p-phenylenediamine was a strong inhibitor in spite of the absence of labile hydrogens. The latter compound was found to form the blue Würster cation at the end of the induction period. Good correlation was found between Hammett sigma values and antioxidant efficiency; the efficiency was increased by electron donating groups which indicates that electron removal is important. It was also found that steric hinderance had no effect on the efficiency of the antioxidant which would probably not be the case if initial attack was on the 0-H or N-H bond.

Walling and Mayahi (48) and Russell (49) have shown that chlorine atoms are complexed in aromatic solvents which modifies their chemical reactivity. Russell further found that t-butoxy radicals complexed to a lesser extent. Both polarizability and electron affinities for peroxy radicals should be greater than for alkoxy radicals. This should be reflected in their aptitude for complex formation.

The mechanism of hydroquinone and peroxy radicals is not completely understood. It is a good inhibitor in hydrocarbon systems even in the presence of metal ions. Bolland and ten Have (50) isolated quinone in the products of hydroquinone autoxidation and proposed that hydrogen abstraction is an important step in the inhibition reaction. Kharasch (51) isolated the 2, 5-disubstituted hydroquinone from reactions between hydroquinone and free radicals. Apparently the radicals added to the aromatic ring in these reactions. Hammond's mechanism of complex formation is not incompatible with the results of inhibition studies involving hydroquinone.

In summary, the mechanism of inhibition in the presence of antioxidants has not yet been definitely formulated. The differences may well be due to more than one type of mechanism occurring, depending on the substrate, antioxidant, solvent and temperature.

IV. Cobalt Ions in Autoxidation Systems

The role of cobalt ions in autoxidation systems appears to be two-fold. The metal ion can react with the substrate to produce radicals and/or it can catalyze the decomposition of hydroperoxides (52).

The kinetics of the decomposition of hydroperoxide have been found (30, 31, 53) to vary, depending on the concentration of both cobalt and hydroperoxide. A number of compounds such as acetic acid, chloroform, carbon tetrachloride and water were found to retard the decomposition (53). Emerson et al (54) studied the chromium catalyzed autoxidation of ethylbenzene and suggested that water complexed with the chromium to reduce its activity.

Bawn (52) and others (35, 53) have observed that oxygen absorption was preceded by a color change from pink to green indicating that the cobalt changed from the +2 to the +3 oxidation state. The decomposition of hydroperoxides by cobalt has been postulated (12, 43, 52) to proceed by the following mechanism:

$$\mathrm{R00H} + \mathrm{Co}^{+3} \longrightarrow \mathrm{R00\cdot} + \mathrm{Co}^{++} + \mathrm{H}^{+} \qquad (33)$$

$$\mathrm{R00H} + \mathrm{Co}^{++} \longrightarrow \mathrm{R0\cdot} + \mathrm{0H}^{-} + \mathrm{Co}^{+3} \qquad (34)$$

where the first step would be rate determining according to the above observation of the green Co^{+3} ion. George et al (29) found that when copper stearate was added to tetralin, much more inhibitor was needed to inhibit the reaction. They proposed that the cobalt catalysis proceeds by a complex formation:

$$\mathrm{ROOH} + \mathrm{M} \rightleftharpoons [\mathrm{ROOH}\cdots\mathrm{M}] \longrightarrow \mathrm{M} + \text{radicals} \tag{35}$$

Uri (10) studied the effect of cobalt salts on methyl stearate and suggested that the major role of the cobalt ion was to act as an oxygen carrier which could then initiate chains:

$$\mathrm{Co}^{++} + \mathrm{O}_2 \longrightarrow \mathrm{CoO}_2\cdot^{++} \tag{36}$$

$$\mathrm{CoO}_2\cdot^{++} + \mathrm{RH} \longrightarrow \mathrm{Co}^{+3}\mathrm{R}^- + \mathrm{HO}_2\cdot \tag{37}$$

$$\mathrm{HO}_2\cdot + \mathrm{RH} \longrightarrow \mathrm{HO}_2\mathrm{H} + \mathrm{R}\cdot \tag{38}$$

In benzaldehyde systems, Bawn and Jolley (55) proposed that cobalt initiated free radicals by the following sequence:

$$\mathrm{Co}^{+3} + \mathrm{RCHO} \longrightarrow \mathrm{Co}^{++} + \mathrm{R\dot{C}O} + \mathrm{H}^+ \tag{39}$$

Blanchard (13) recently studied the effects of cobalt in cumene systems using acetic acid as a solvent. He found that little or no decomposition of hydroperoxide occurred at cobalt concentrations below 4.1 m*M* but that rapid decomposition occurred above this concentration. However, the use of acetic acid as a solvent might have complicated the results (53). Initiation in the absence of a free radical source was said to be due to the catalytic decomposition of small amounts of hydroperoxide present in the system or from reaction of cobalt and impurities.

It appears that the role of metal ions in autoxidation systems is dependent on the experimental conditions. Whether cobalt acts only to decompose hydroperoxides in aralkyl hydrocarbon systems or initiates chains by reacting with oxygen has not been adequately answered.

EXPERIMENTAL

I. General

Kinetic studies herein reported were made by two methods. The first method was that of induction period analysis. Initiator, inhibitor and substrate were placed in a sealed flask filled with oxygen at one atmosphere pressure and kept in a constant temperature bath. The reaction flask was connected to an automatic recorder that plotted pressure versus time. The induction period was determined from this data by means of graphical intercepts.

The second method was used in systems where no appreciable induction period occurred. In these cases the amount of oxygen taken up by the system over a specified period of time was measured by the recorder.

Both of the above methods were used to examine the effects of various parameters on the rates of the processes under study. The parameters that were examined included: concentration of initiators, concentration of inhibitors, concentration of additives and temperature.

II. Purification of Tetralin

Tetralin (1, 2, 3, 4-tetrahydronaphthalene) was chosen as the substrate because it oxidizes at a reasonable rate at the temperatures employed in this study (60 to 90°) and its hydroperoxide is stable at these temperatures.

Fisher Scientific Company's Purified grade tetralin was found to have a refractive index of 1.5368 at 20°. It was further purified by a batch process similar to that used by Lloyd (2).

A 13 l. round bottom flask was filled with 10 l. of tetralin which was clear and colorless. The tetralin was washed six times with 500 ml. portions of concentrated reagent grade sulfuric acid. Each wash was stirred vigorously for one hour, allowed to separate and the lower layer was siphoned off. The initial raffinates were dark brown and the last was clear and pale yellow.

The tetralin was then washed with one l. of distilled water, one l. of 1.0 M sodium hydrogen carbonate, and finally with four successive one l. portions of distilled water. The pH of the mixture was 7 after the second washing with water. At this time the tetralin was cloudy and colorless due to the presence of water.

The wet tetralin was then dried by adding anhydrous reagent grade sodium sulfate and stirring the mixture for 24 hours. The tetralin was clear and colorless.

The tetralin was filtered to remove the sodium sulfate and 20 g. of sodium wire were placed into the flask containing the hydrocarbon. It was found that applying a vacuum to the system by means of a water aspirator markedly increased the drying rate and the effectiveness of the operation. The flask was allowed to stand for 24 hours with occasional swirling.

The tetralin was then filtered and passed through a four foot by one inch column, the lower half of which was packed with freshly activated, 28-200 mesh silica gel and the upper half with alumina. The flow rate was approximately 50 drops per minute. The pure tetralin was collected under prepurified nitrogen which had passed through a copper furnace at 350°, concentrated sulfuric acid and drierite. The refractive index of the tetralin was 1.5413 at 20°. This is in good agreement with the literature value of 1.54135 at 20° (56).

This tetralin was distilled under nitrogen through a 100 cm. heated column packed with glass helices with an automatic take-off head set at a reflex ratio of 10:1. The refractive index of the center cut was 1.5413 at 20°.

Analysis of the distilled tetralin by gas chromotography showed a small unknown peak possibly due to tetralin hydroperoxide. An estimate of the concentration of this impurity from the area under the peak showed its concentration to be about six parts in one thousand.

A sample of the tetralin taken prior to distillation showed this same peak and by similar means its concentration was found to be three parts in one thousand.

The infrared spectra of both samples were found to conform exactly to that of an A. P. I. Research Project 44 (56) spectra of 99.86±0.06 mole per cent tetralin. The samples were run in 0.025 mm. cells and there was no peak at 2.9 microns which indicated that no appreciable amounts of water or tetralin hydroperoxide was present.

From these results it was concluded that distillation was not necessary and the tetralin was used after it passed through the chromotographic column. The bulk of the tetralin was stored in one-gallon brown bottles under nitrogen in a refrigerator. Care was taken to exclude oxygen and light from the purified tetralin.

III. Other Chemicals

A. Tetralin hydroperoxide (1, 2, 3, 4-tetrahydronaphthalene-1-hydroperoxide)

The tetralin hydroperoxide (THP) was prepared by the autoxidation of tetralin using AIBN as the initiator. Approximately 500 ml. of pure tetralin was added to a two-necked flask fitted with a reflex condenser and a fritted glass bubbling tube. This was placed in an 80° water bath and 0.1 g. of AIBN was added to the tetralin. Oxygen gas was bubbled through the hydrocarbon for 24 hours.

In order to separate the THP from the tetralin, the reaction solution was vacuum distilled at 0.10 mm. of mercury. The temperature was kept below 80°. This removed most of the tetralin and left a viscous light brown residue. The residue was placed in a liquid-liquid extractor and the THP was extracted with pentane for 12 hours.

The extract was then placed in a refrigerator and in a few hours, white crystals of THP were formed along with some yellow plates. Six recrystallizations resulted in pure white crystals, melting at 55.0-56.0°. The melting point of the pure compound is 56.0° (57). The yield was 18.3 g. An infrared spectrum was taken which agreed with the spectrum reported in the literature (58).

An iodine-thiosulfate titration was made on two samples of the THP and this material was found to contain approximately 99 per cent hydroperoxide. The compound was kept under refrigeration in a desiccator.

B. Cobalt (II) naphthenate (cobalt (II) cyclohexane-carboxylate)

Cobalt (II) naphthenate was obtained from the Noudex Corporation as "Noudex Cobalt 6." It contained approximately six per cent cobalt as cobalt (II) naphthenate in naphthenic acid. A solution of approximately 5×10^{-1} M cobalt in spectroanalyzed grade benzene was prepared and polarographically* analyzed. One ml. of this solution was made up to a liter in a solution containing 0.1 M pyridine and 0.1 M pyridinium chloride. Gelatin (0.01 per cent) was added to suppress the wave maximum. The concentration of the solution was found to be 4.75×10^{-1} M cobalt. There were no transition metal impurities found in the solution. This solution was then diluted with benzene to give a stock solution of 9.50×10^{-3} M cobalt.

C. 2,2'-Azobisisobutyronitrile

This compound, commonly called AIBN, was obtained from Eastman Organic Chemicals, White Label grade. It was a white crystalline solid and the melting point was 102-103°. The reported melting point of pure AIBN was 103-104° (59). This compound was stored in a desiccator under refrigeration and was used without further purification.

---

*The writer is indebted to Dr. J. M. Pearce for the polarographic analysis of the cobalt solution.

D. Dibutylcresol (2, 6-di-tert-butyl-4-methylphenol)

Dibutylcresol (DBC) was obtained from Shell Chemical Corporation, C.P. Edible grade, under the trade name of Ionol. The compound was a white granular solid with a melting point of 69-70°. Blanchard (13) reported the melting point of the pure compound to be 70°. The DBC was stored in the dark and used without further purification.

E. Hydroquinone

J. T. Baker Chemical Company, Purified, Lot 7301, hydroquinone (HQ) was a white crystalline solid. The melting point of the compound was 170-171°. The reported melting point of the pure compound was 170.5° (60). The HQ was stored in the dark and used without further purification.

F. Quinone (p-benzoquinone)

This compound was obtained from Eastman Chemical Products, 99.82 per cent assay, and the crystals were brown. The quinone was purified by sublimation and gave bright yellow crystals with a melting point of 114.5-115.0°. The reported melting point was 115.7° (60). The quinone was stored under refrigeration.

G. Quinhydrone (benzoquinhydrone)

The dark green crystals of quinhydrone, obtained from Eastman Organic Chemicals, melted at 170-171°. The literature reported a melting point of 171° (60). The compound was used without further purification.

H. p-Methoxyphenol

This white crystalline compound was recrystallized once from water and four times from dry benzene. The crystals were collected by vacuum filtration and dried for 24 hours at 5 mm. of mercury. The melting point of the pure crystals was 52.5-53.0°. The reported melting point was 53° (60). The purified compound was stored under refrigeration.

All other reagents and solvents used were C. P. grade or higher.

IV. Apparatus

The apparatus used in this investigation consisted of a reaction flask connected by capillary tubing to a pressure recorder. The flask was immersed in a constant temperature bath and the reactants were stirred by means of a magnetic stirrer.

The reaction flask was constructed from a 2 l. Erlenmeyer flask fitted with a male standard taper joint. The top contained a glass tube with a stopcock which was used to flush the system with oxygen. A side arm with a ball joint was used to connect the flask to the pressure recorder. The total volume of this system was 2,065 ml.

The pressure changes in the flask were measured by a Foxboro absolute pressure recorder (Foxboro Company, model 40). The recorder consisted of a stainless steel bellows connected to a pen which recorded pressure as a function of time on a circular chart. The instrument recorded pressure changes between 360 and 760 mm. of mercury. The pressure could be read to the nearest millimeter and the time to the nearest minute with reasonable accuracy.

The water bath was heated by a 1,000-watt heating element and the temperature was controlled by a preset thermoregulator (H-B Instrument Company, model LER-1281-Al). An electronic relay (Lumenite Electronic

Corporation, model 7910-A) connected the heating element and the thermoregulator. This system kept the temperature of the bath constant within ±0.1°. The entire bath was insulated and a cover was put over the top to keep out light. The bath temperatures were checked with a thermometer (number 61090) standardized by the National Bureau of Standards. The nominal and true temperatures are given in Table 1.

The reaction solution was stirred at a constant rate by means of a Bodine constant-speed 300 r.p.m. motor. The motor was fitted with an alnico magnet which drove a standard teflon clad magnet in the reaction flask.

TABLE 1

TEMPERATURE CALIBRATION OF BATH

Nominal Temperature*	True Mean Temperature
60°	60.2_3°
70°	70.2_8°
80°	80.3_5°

*For convenience, nominal temperatures are used throughout the text. The true mean temperatures are used in all calculations.

V. Sample Preparation

In general, samples were prepared by putting the additives and 100 ml. of tetralin into the flask and flushing the system with oxygen (3.3 l. per minute) for five minutes. The flask was then immersed in the constant temperature bath and the magnetic stirrer and recorder were turned on. The stopcock was left open for the first 90 seconds to allow the system to reach thermal equilibrium.

The solid additives were weighed out on glassine paper using a Mettler balance (sensitivity ±0.02 mg.) and the method of differences. The additives were put into the flask and 100 ml. of tetralin were added by means of a pipette. Initiators were always put into the flask last.

Cobalt (II) naphthenate solution was delivered with a 0.25 ml. syringe. The concentration of the cobalt solution was 9.50×10^{-3} $\underline{M}$, and 0.25 ml. of this solution in 100 ml. of tetralin gave a resultant concentration of 2.38×10^{-5} $\underline{M}$ cobalt.

The ground glass joints were then lubricated with D-C Silicone High-Vacuum Grease, and the flask was flushed with oxygen. During the oxygen flush, the reactants were stirred to effect solution of the additives in the tetralin.

To avoid contamination from preceding runs, all equipment was thoroughly cleaned prior to use. The flask was rinsed three times with acetone, once with water, once with detergent solution, five times with tap water, three times with distilled water and four times with acetone. The contents were shaken vigorously during each rinse. Pipettes were cleaned with four charges of acetone. The syringe used for the cobalt addition was rinsed four times with benzene and twice with acetone. Neither chromic acid cleaning solution nor sulfuric acid was used to clean any equipment.

VI. Interpretation of a Typical Autoxidation Run

The following run will illustrate the treatment of the raw experimental data. In this run, 97.90 mg. of AIBN, 21.40 mg. of DBC and 100 ml. of tetralin were put into the reaction flask. The resultant concentration of AIBN was 5.96×10^{-3} M and that of DBC was 0.971×10^{-3} M. The sample was autoxidized at 60° under an oxygen atmosphere.

The pressure-time data are given in Table 2 and plotted in Figure 1. The length of the induction period (t_i) is obtained from Figure 1 by drawing straight lines before and after the pressure drop. The intercept of these two lines is taken as the time at which the induction period is over. From the graph, the t_i for this run is 12.50 hours.

A second method may be used to determine the intercept of these two lines (2). The end of the induction period is the time at which the third derivative of pressure with respect to time falls from a positive value to zero. Variations by these two methods are generally small and induction periods reported herein are obtained by the method of graphical intercepts.

TABLE 2

DATA FOR A TYPICAL AUTOXIDATION RUN

(100 ml. tetralin, 6.14 mM AIBN, 1.00 mM DBC, 60°, 1 atm. 0_2)

Time, hrs.	Pressure, mm.
1:00	376
2:00	376
3:00	376
4:00	376
5:00	376
6:00	376
7:00	376
8:00	376
9:00	376
10:00	376
11:00	376
12:00	375
13:00	366
14:00	347
15:00	328
16:00	308

end of run

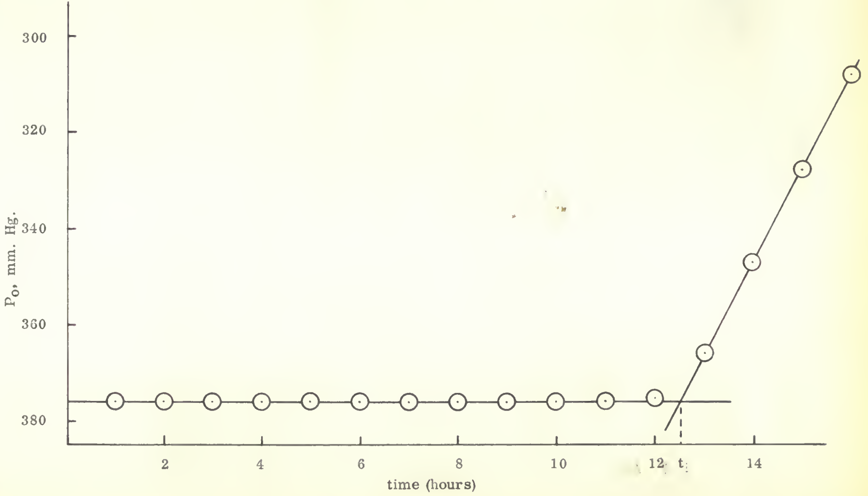


Figure 1. Plot of oxygen pressure versus time for a typical autoxidation run

RESULTS

The experimental results obtained in this kinetic study will be presented in three sections. The first section summarizes studies using a non-branching initiator, 2, 2'-azobisisobutyronitrile (AIBN), and two phenolic inhibitors, hydroquinone (HQ) and dibutylcresol (DBC). The second section contains the results of studies on a system with a branching catalyst, cobalt (II) naphthenate, tetralin hydroperoxide, HQ and DBC. The third section reports the results in systems containing other additives with either cobalt catalyst or AIBN initiator.

I. The System 2, 2'-Azobisisobutyronitrile and Inhibitor in Tetralin

The results in this section show the concentration effects of inhibitor and AIBN initiator on the length of the induction period. Two inhibitors were investigated; HQ which is a non-hindered phenol and DBC, a sterically hindered phenol. Sets of runs were made with each inhibitor at 60°, 70° and 80°.

The main reasons for making these runs are:

1. to determine the efficiency (α) of AIBN initiator;
2. to calculate the stoichiometry of HQ;
3. to elucidate one phase of the mechanism of inhibition, i. e., the fact that the inhibitors operate by scavenging radicals.

The first two factors will be discussed in this section and the last deferred to the Discussion section.

The AIBN initiator is known to decompose spontaneously by first-order kinetics at the temperatures investigated in this study. Since the rate constant for the decomposition is known, the number of radicals produced during the induction period may be calculated. The inhibitor stoichiometry can be found by comparing the moles of radicals produced and the moles of inhibitor consumed.

The number of radicals produced by the initiator during the induction period can be found from the rate law for AIBN decomposition.

$$\frac{-d\left[\mathrm{AIBN}\right]}{dt} = k_1\left[\mathrm{AIBN}\right] \qquad (40)$$

where k_1 is the specific rate constant for the decomposition of AIBN.

From this relation, equation 41 has been derived which gives the number of radicals (Σ R) produced during the induction period.

$$\Sigma R = 2\left[\mathrm{AIBN}\right]_o \left[1 - e^{-k_1 t_1}\right] \qquad (41)$$

where $\left[\mathrm{AIBN}\right]_o$ is the initial concentration of initiator and t_1 equals the length of induction period in seconds.

The values for k_1 used in this work are calculated from the data of Van Hook and Tobolsky (17) and are:

k_1 at $60.2_3{}^{\circ}$ = 9.73×10^{-6} sec.$^{-1}$

k_1 at $70.2_8{}^{\circ}$ = 5.89×10^{-5} sec.$^{-1}$

k_1 at $80.3_5{}^{\circ}$ = 1.41×10^{-4} sec.$^{-1}$

In order to determine the apparent stoichiometry, the Σ R versus the inhibitor concentration has been plotted for those series where the AIBN concentration is constant. The least squares slope and standard deviation of these plots have been calculated by the method of Youden (61). The slope of the line gives the apparent stoichiometry of the inhibitor. For those series where the AIBN concentration was varied, the apparent stoichiometry has been calculated by dividing the Σ R by the concentration of inhibitor for each run.

A. Hydroquinone in 2, 2'-azobisisobutyronitrile systems

Effect of hydroquinone concentration at 60°. The effect of hydroquinone concentration on induction period at 60° was investigated by a series of four runs at a constant AIBN concentration of 5.96 m*M*. The HQ concentration was varied from 0.486 to 1.94 m*M*. The results of this series are shown in Table 3. The number of radicals (Σ R) produced during the induction period is plotted versus HQ concentration in Figure 2. The data describe a good straight line with a slope of 2.24 radicals per molecule of HQ with a standard deviation of ±0.05.

Effect of hydroquinone concentration at 70°. A series of seven kinetic runs was made at 70° at a constant AIBN concentration of 4.22 m*M* and with HQ concentrations ranging from 0.971 to 3.88 m*M*. The results appear in Table 4 and are plotted in Figure 3. The slope of the line is 1.89 radicals per molecule of HQ with a standard deviation of ±0.14.

Effect of hydroquinone concentration at 80°. A third series of runs was made at 80° with a constant AIBN concentration of 5.96 m*M*. The HQ concentration was increased from 1.94 to 4.86 m*M*. The results are given in Table 5 and plotted in Figure 4. The points lie in a line with a slope of 2.18 radicals per molecule of HQ and have a standard deviation of only ±0.02.

The linearity of the plots indicates that the destruction of HQ is determined by the rate of radical formation from AIBN. The radical that reacts with the inhibitor is presumably the tetralylperoxy radical formed by the following sequence:

TABLE 3

EFFECT OF HYDROQUINONE ON INDUCTION PERIOD AT 60°

(100 ml. tetralin, 5.96 mM AIBN, 1 atm. 0_2)

$[HQ]_o$ x 10^3	t_i hours	ΣR x 10^3
0.486	2.60	1.04
0.971	5.35	2.04
1.46	8.60	3.09
1.94	12.80	4.32

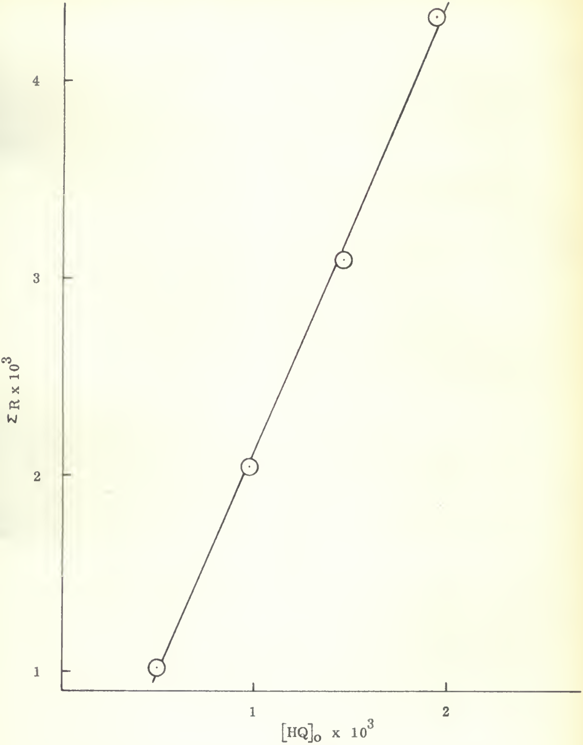


Figure 2. Plot of ΣR versus $[HQ]_o$ at 60° (100 ml. tetralin, 5.96 m$\underline{M}$ AIBN, 1 atm. O_2)

TABLE 4

EFFECT OF HYDROQUINONE ON INDUCTION PERIOD AT 70°

(100 ml. tetralin, 4.22 m_M_ AIBN, 1 atm. 0_2)

$[HQ]_o$ x 10^3	t_i hours	ΣR x 10^3
0.971	1.80	1.88
1.94	4.38	3.87
1.94	4.33	3.84
2.33	6.40	5.00
2.33	6.70	5.14
2.91	8.30	5.81
3.88	14.63	7.36

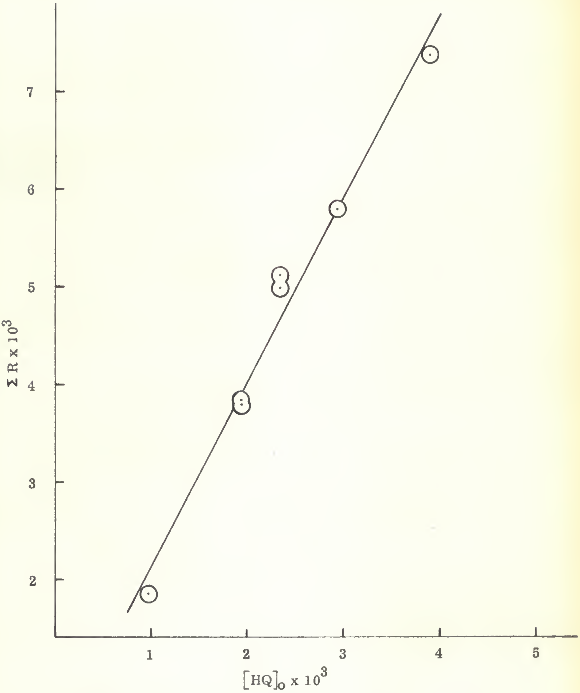


Figure 3. Plot of Σ R versus $[HQ]_o$ at 70° (100 ml. tetralin, 4.22 m$\underline{M}$ AIBN, 1 atm. O_2)

TABLE 5

EFFECT OF HYDROQUINONE ON INDUCTION PERIOD AT 80°

(100 ml. tetralin, 5.96 mM AIBN, 1 atm. O_2)

$[HQ]_0$ $\times 10^3$	t_i hours	ΣR $\times 10^3$
1.94	1.13	5.21
2.91	1.87	7.37
3.88	3.13	9.49
4.86	6.90	11.56

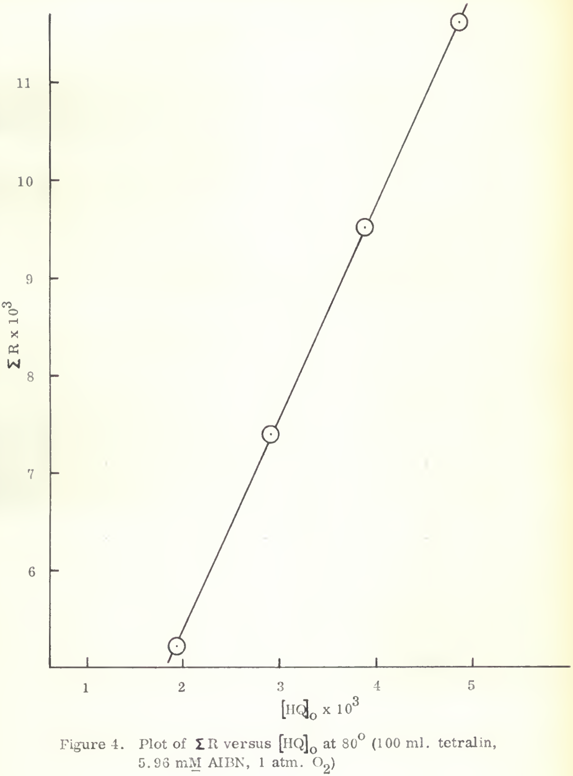


Figure 4. Plot of ΣR versus $[HQ]_o$ at 80° (100 ml. tetralin, 5.96 m$\underline{M}$ AIBN, 1 atm. O_2)

$$\mathrm{AIBN} \longrightarrow \mathrm{R\cdot} \qquad (42)$$

$$\mathrm{R\cdot} + \mathrm{TH} \longrightarrow \mathrm{T\cdot} + \mathrm{RH} \qquad (43)$$

$$\mathrm{T\cdot} + \mathrm{0_2} \longrightarrow \mathrm{T00\cdot} \qquad (44)$$

where R· is the radical from AIBN decomposition, TH is the tetralin substrate, T· is the tetralyl radical and T00· is the tetralylperoxy radical.

The figures obtained for the apparent stoichiometry show good agreement and give an average value of 2.1 radicals stopped per molecule of HQ.

B. Dibutylcresol in 2,2'-azobisisobutyronitrile systems

Effect of dibutylcresol concentration at 60°. A series of four kinetic runs was made at 60° to study the effect of DBC concentration on the induction period. The DBC concentration ranged from 0.486 to 1.46 m*M* and the AIBN concentration was kept constant at 5.96 m*M*. The results of this series are presented in Table 6 and plotted in Figure 5. The points describe a line with a slope of 4.10 radicals per molecule of DBC and have a standard deviation of ±0.17.

Effect of dibutylcresol at 70°. A second series of five runs was made at 70°. In this series, both AIBN and DBC concentrations were varied. The data is summarized in Table 7 and the average apparent stoichiometry is 3.69 radicals per molecule of DBC.

Effect of dibutylcresol at 80°. A series of four runs was made at 80° and again both AIBN and DBC concentrations were varied. The results of these runs are in Table 8 and the average apparent stoichiometry is 3.55 radicals per molecule of DBC.

TABLE 6

EFFECT OF DIBUTYLCRESOL ON INDUCTION PERIOD AT 60°

(100 ml. tetralin, 5.96 mM AIBN, 1 atm. 0_2)

$[DBC]_0$ x 10^3	t_i hours	ΣR x 10^3
0.486	5.45	2.07
0.728	8.45	3.05
0.971	12.50	4.23
1.46	20.20	6.04

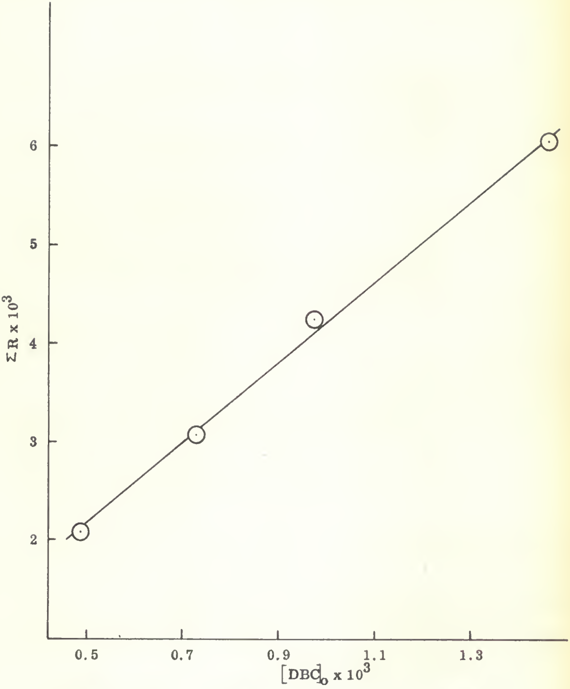


Figure 5. Plot of ΣR versus $[DBC]_0$ at 60° (100 ml. tetralin, 5.96 m$\underline{M}$ AIBN, 1 atm. O_2)

TABLE 7

EFFECT OF DIBUTYLCRESOL ON INDUCTION PERIOD AT 70°

(100 ml. tetralin, 1 atm. 0_2)

$[AIBN]_o$ x 10^3	$[DBC]_o$ x 10^3	t_i hours	ΣR x 10^3	Apparent Stoichio.
1.80	0.927	17.2	3.28	3.54
2.43	0.971	9.25	3.53	3.64
3.05	0.927	6.05	3.50	3.78
3.39	0.934	5.18	3.50	3.75
3.88	0.927	4.20	3.45	3.72
			Average	3.69

TABLE 8

EFFECT OF DIBUTYLCRESOL ON INDUCTION PERIOD AT 80°

(100 ml. tetralin, 1 atm. O_2)

$[AIBN]_o$ x 10^3	$[DBC]_o$ x 10^3	t_i hours	ΣR x 10^3	Apparent Stoichio.
3.40	0.971	1.43	3.51	3.61
3.40	1.94	8.30	6.70	3.45
5.96	1.94	1.73	6.97	3.59
5.96	2.91	3.92	10.30	3.54
			Average	3.55

Runs with short induction periods. In an effort to further investigate the DBC system, a series of runs having short induction periods was made. For these runs, destruction of inhibitor by sources other than those from AIBN should be minimized. The results of this series are presented in Table 9 and show good agreement with the previous results obtained in DBC systems. The average values for the apparent stoichiometry from the two sets of data at 60^{o}, 70^{o} and 80^{o} are 4.0, 3.7 and 3.6 radicals per molecule of DBC. These values will be used in calculations of initiator efficiencies.

The HQ and DBC studies have shown that the inhibitor is used up by radicals produced by the decomposition of AIBN. However, product isolation studies indicate that the stoichiometry of DBC is 2.0. This point will be discussed in the next section.

C. Inhibitor stoichiometry and radical efficiencies

In the method developed in the previous section for determining the apparent stoichiometry, an implicit assumption was made that each molecule of AIBN produced two radicals. A number of workers (14, 62-65) have found that the radical producing efficiency is less than 100 per cent and dependent on the system studied.

The reason suggested for this low efficiency is that when the radicals are produced they are surrounded by a solvent "cage" and are close proximity for a finite time. Hence the radicals can either recombine or diffuse apart. The initiator efficiency (α) is the fraction of radicals that diffuse apart. This process can be represented as follows:

TABLE 9

APPARENT STOICHIOMETRY FROM RUNS WITH SHORT INDUCTION PERIODS

(100 ml. tetralin, 1 atm. 0_2)

Temp.	$[\mathrm{AIBN}]_o$ x 10^3	$[\mathrm{DBC}]_o$ x 10^3	t_1 hours	Apparent Stoichio.
60	15.50	0.388	1.45	3.92
60	19.40	0.486	1.37	3.74
70	6.80	0.486	1.00	3.66
70	7.77	0.971	2.00	3.92
70	13.60	0.971	1.03	3.78
80	3.40	0.971	1.43	3.61
80	5.96	1.94	1.73	3.51

$$\text{AIBN} \longrightarrow (2\text{R}\cdot) + \text{N}_2 \qquad (45)$$

$$(2\text{R}\cdot) \longrightarrow 2\text{R}\cdot \qquad (46)$$

$$(2\text{R}\cdot) \longrightarrow \text{R-R} \qquad (47)$$

where the parentheses are used to designate radicals still in the solvent "cage".

Utilizing this notion of initiator efficiency in radical production, the actual stoichiometry may be found by multiplying the apparent stoichiometry by the initiator efficiency or:

$$S = (A)\ (\alpha) \qquad (48)$$

where S is the actual stoichiometry, A is the apparent stoichiometry and α is the initiator efficiency.

In order to calculate the actual stoichiometry of HQ we must know the value of α. Hammond and co-workers (7) and Campbell and Coppinger (65) have reported that the stoichiometry of DBC is 2.0 radicals per molecule. Using this value and the apparent stoichiometries obtained in this study we can calculate the α values for AIBN in tetralin substrate. The initiator efficiencies of AIBN are 0.50, 0.54 and 0.56 at 60°, 70° and 80° respectively. Hammond, Sen and Boozer (14) have reported α values for AIBN in chlorobenzene, benzene and nitrobenzene that range from 0.57 to 0.75.

The stoichiometry of HQ can now be calculated by using the above derived α values and equation 48. The calculated stoichiometries of HQ at 60°, 70° and 80° are 1.1, 1.0 and 1.2 or an average of 1.1 radicals per molecule of HQ.

II. The System Cobalt (II) Naphthenate, Tetralin Hydroperoxide and Inhibitors in Tetralin

The effects of hydroquinone, dibutylcresol and tetralin hydroperoxide concentrations on the length of the induction period are presented in this section. These runs were made at 70° in the presence of cobalt (II) naphthenate. Cobalt acts as a branching catalyst in the presence of the peroxide to initiate the radical chain process.

This section is subdivided into two parts according to the inhibitor used in the system. Part A presents the results of studies conducted with HQ and Part B reports those studies made in the presence of DBC.

A. Hydroquinone in cobalt systems

Effect of hydroquinone concentration. A series of five kinetic runs was made at a constant cobalt concentration of 2.38×10^{-5} M and a constant THP concentration of 2.00 mM. The HQ concentration was varied from 1.00 to 1.50 mM. The results are shown in Table 10 and a plot of t_i versus $[HQ]_0^3$ is given in Figure 6. The slope of the line is 9.0 and the standard deviation is ±0.9.

The run made with an initial HQ concentration of 1.50 mM was taken off after 45 hours since the induction period had not ended. As is evident from the data, the length of the induction period increased sharply with inhibitor concentration.

TABLE 10

EFFECT OF HYDROQUINONE ON INDUCTION PERIOD

(100 ml. tetralin, 2.00 mM THP, 2.38 x 10^{-5} M cobalt (II) naphthenate, 70°, 1 atm. 0_2)

$[HQ]_o$ x 10^3	$[HQ]_o^3$ x 10^3	t_1 hours
1.00	1.000	0.97
1.10	1.331	2.00
1.25	1.953	8.18
1.35	2.460	13.6
1.50		45

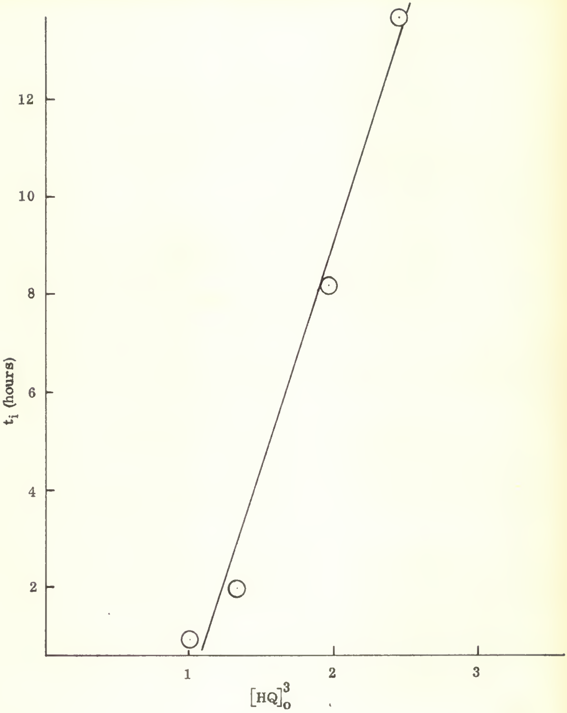


Figure 6. Plot of t_i versus $[HQ]_0^3$ (100 ml. tetralin, 2.00 m$\underline{M}$ THP, 2.38×10^{-5} $\underline{M}$ cobalt (II) naphthenate, 70°, 1 atm. O_2)

A second series of runs was made to show the effect of HQ on the induction period when the initial concentration of THP is doubled. The results are presented in Table 11. A ln - ln plot of the data shown in Figure 7 gives a straight line with a slope of 3.2 and a standard deviation of ± 0.2.

B. Dibutylcresol in cobalt systems

Effect of dibutylcresol concentration. Five runs were made at a constant cobalt concentration of 2.38×10^{-5} M and a constant THP concentration of 2.00 mM. The concentration of DBC was varied from 1.80 to 2.50 mM and the effects on the induction periods are presented in Table 12. A plot of ln t_1 versus ln $[\mathrm{DBC}]_0$ is given in Figure 8. The points describe a line with a slope of 16.4 and a standard deviation of ±5.1.

A second series of nine runs was made at a THP concentration that was four times greater than that in the above case. The DBC concentration was varied from 2.00 to 8.80 mM. The data from this series are shown in Table 13 and a plot of t_1 versus ln $([\mathrm{THP}]_0 - [\mathrm{DBC}]_0)$ is given in Figure 9. A least squares fit of the data gives a slope of -5.6 and a standard deviation of ±0.6.

Effect of tetralin hydroperoxide concentration. A series of four runs was made to study the effect of THP concentration on induction period. The DBC concentration was 2.35 mM and the cobalt concentration was 2.38×10^{-5} M. The results are shown in Table 14 and plotted in Figure 10. Inspection of the results shows that the induction period had a

TABLE 11

EFFECT OF HYDROQUINONE ON INDUCTION PERIOD

(100 ml. tetralin, 4.00 m*M* THP, 2.38×10^{-5} *M* cobalt (II) naphthenate, 70°, 1 atm. O_2)

$[HQ]_o$ x 10^3	ln $[HQ]_o$ + 6.91	t_i hours	ln t_i
0.75	-0.288	0.68	-0.386
1.00	0.000	2.43	0.888
1.25	0.223	4.64	1.535
1.50	0.405	7.75	2.048
2.00	0.693	17.6	2.836
2.50		39	

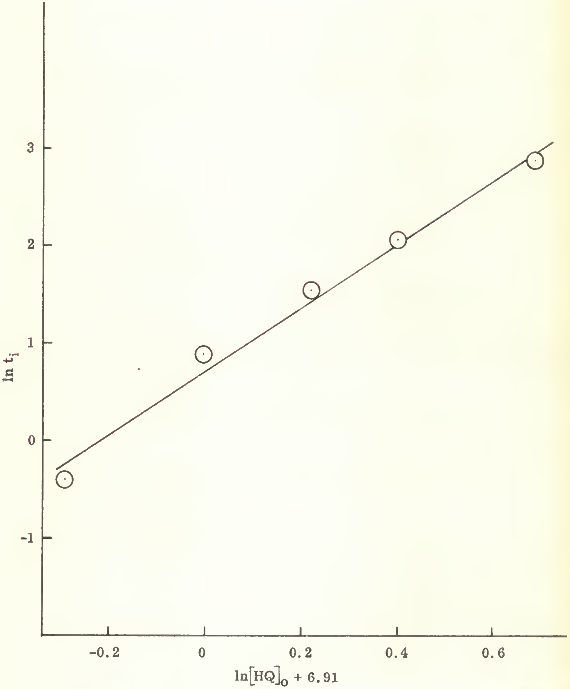


Figure 7. Plot of ln t_i versus $[HQ]_o$ (100 ml. tetralin, 4.00 mM THP, 2.38×10^{-5} M cobalt (II) naphthenate, 70°, 1 atm. O_2)

TABLE 12

EFFECT OF DIBUTYLCRESOL ON INDUCTION PERIOD

(100 ml. tetralin, 2.00 m$\underline{M}$ THP, 2.38×10^{-5} $\underline{M}$ cobalt (II) naphthenate, 70°, 1 atm. O_2)

$[DBC]_o$ $\times 10^3$	$\ln [DBC]_o$ + 6.91	t_i hours	$\ln t_i$
1.80	0.588	0.23	-1.470
2.00	0.693	0.37	-0.994
2.20	0.788	1.79	0.582
2.35	0.854	21.95	3.090
2.50		72	

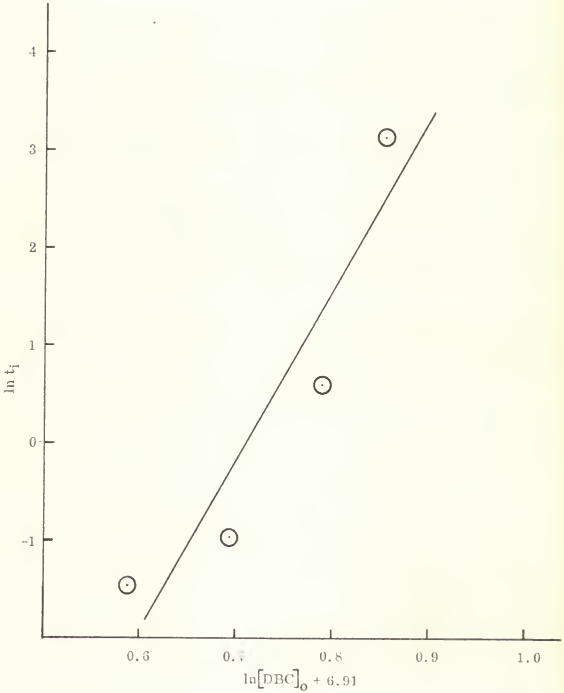


Figure 8. Plot of ln t_i versus ln$[DBC]_o$ (100 ml. tetralin, 2.00 m$\underline{M}$ THP, 2.38 x 10^{-5} $\underline{M}$ cobalt (II) naphthenate, 70^o, 1 atm. O_2)

TABLE 13

EFFECT OF DIBUTYLCRESOL ON INDUCTION PERIOD

(100 ml. tetralin, 8.00 $m\underline{M}$ THP, 2.38×10^{-5} $\underline{M}$ cobalt (II)
naphthenate, 70°, 1 atm. O_2)

$[DBC]_o$ x 10^3	$[THP]_o - [DBC]_o$ x 10^3	$\ln([THP]_o - [DBC]_o)$ + 6.91	t_i hours
2.00	6.00	1.792	0.16
2.50	5.50	1.705	0.37
3.00	5.00	1.609	0.95
3.25	4.75	1.558	0.95
3.50	4.50	1.504	1.73
3.70	4.30	1.459	1.35
4.50	3.50	1.252	2.88
5.00	3.00	1.099	8.57
8.80	-0.80		48.0

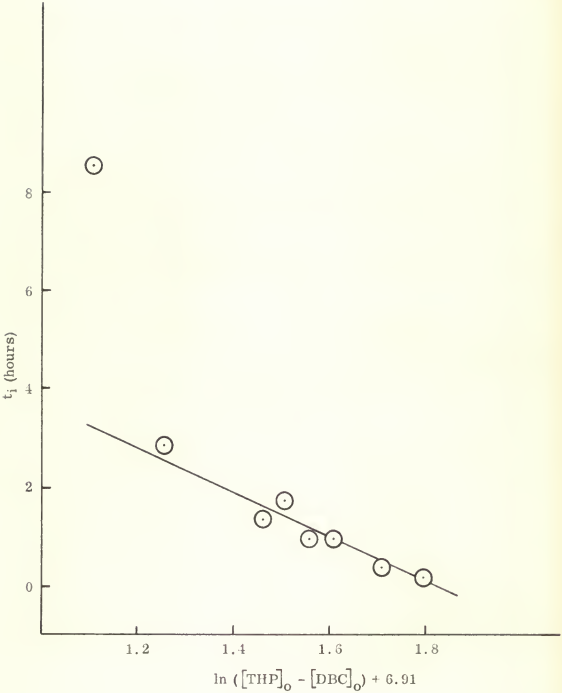


Figure 9. Plot of t_i versus ln ([THP]$_o$ - [DBC]$_o$) (100 ml. tetralin, 8.00 m$\underline{M}$ THP, 2.38×10^{-5} $\underline{M}$ cobalt(II) naphthenate, 70°, 1 atm. O_2)

TABLE 14

EFFECT OF TETRALIN HYDROPEROXIDE ON INDUCTION PERIOD

(100 ml. tetralin, 2.35 mM DBC, 2.38 x 10^{-5} M cobalt (II) naphthenate, 70°, 1 atm. O_2)

$[THP]_o$ x 10^3	$\ln [THP]_o$ + 6.91	t_i hours
2.00	0.693	21.95
2.20	0.788	0.58
2.50	0.916	0.30
3.00	1.099	0.33

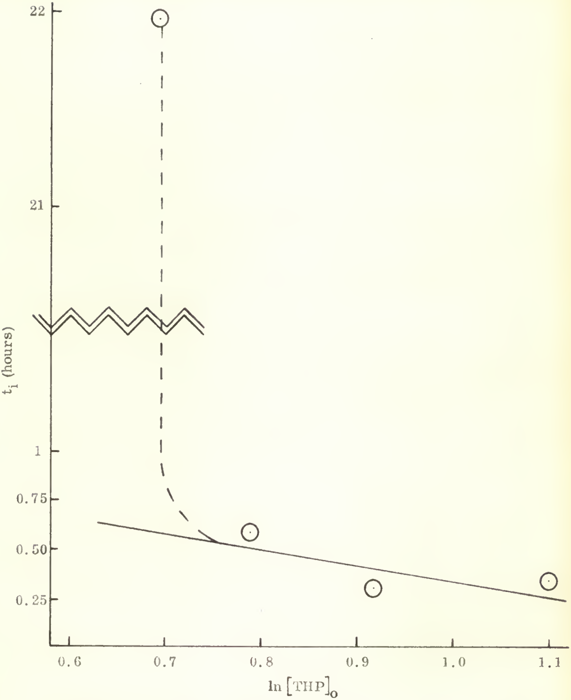


Figure 10. Plot of t_i versus ln $[THP]_o$ (100 ml. tetralin, 2.35 m$\underline{M}$ DBC, 2.38×10^{-5} $\underline{M}$ cobalt (II) naphthenate, 70°, 1 atm. O_2)

strong dependency on the concentration of THP. A change in the induction period of over 21 hours was effected by 0.20 m*M* of THP. Three of the runs exhibited very short induction periods and the fourth showed a long induction period. The least squares slope of the line for the three short runs is -0.74 with a standard deviation of ±0.65.

III. Cobalt (II) Naphthenate and 2, 2-Azobisisobutyronitrile with Other Additives

This section is divided into two parts. The first part reports the results of studies in systems catalyzed by cobalt (II) naphthenate and the second gives the results of systems initiated by AIBN. The additives used in this section are: water, quinone, THP, 1,4-dimethoxybenzene, p-methoxyphenol, DBC and quinhydrone.

The majority of runs in this section did not exhibit induction periods. For these cases the oxygen pressure drop for one hour was recorded after allowing 15 minutes for the system to reach equilibrium.

A. Cobalt (II) Naphthenate Systems

Effect of cobalt concentration. A series of six kinetic runs was made with cobalt concentrations ranging from 0.475 to 2.38 x 10^{-5} M. The results are in Table 15 and a plot of ln initial cobalt concentration is given in Figure 11. The first five points describe a good straight line with a slope of 0.59 and a standard deviation of ±0.01.

This indicates that the cobalt dependency in the following equation is approximately half-order.

$$\text{Rate} = k\ [\text{Co}]_0^{0.6} \tag{49}$$

Lloyd (2) found the dependency to be 0.54 and also observed a levelling effect at higher cobalt concentrations. The purpose in making

TABLE 15

EFFECT OF COBALT (II) NAPHTHENATE ON RATE OF OXYGEN UPTAKE

(100 ml. tetralin, 70°, 1 atm. 0_2)

$[Co]_0$ x 10^5	ln $[Co]_0$ + 11.5	Rate mm. 0_2/hr.	ln Rate
0.475	-0.750	75	4.317
0.950	-0.051	112	4.718
0.950	-0.051	113	4.727
1.19	0.174	129	4.860
1.19	0.174	131	4.875
2.38	0.867	140	4.942

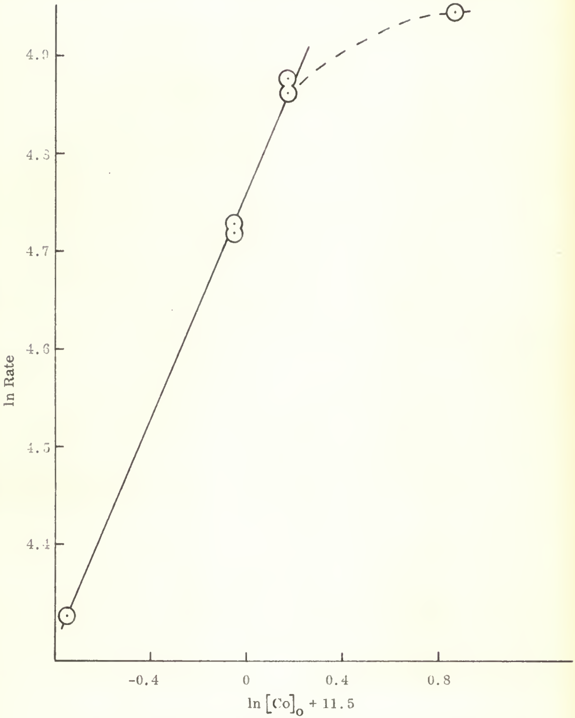


Figure 11. Plot of ln Rate versus ln $[Co]_0$ (100 ml. tetralin, 70°, 1 atm. O_2)

this series was to determine the magnitude of the pressure drop so it could be compared to the following systems. The series also shows that the reproducibility of the method is good.

Effect of water concentration. Three runs were made at a constant cobalt concentration of 0.95×10^{-5} M. The water concentration was varied from 55.4 to 5.54 mM and the effect on the rate of oxygen taken up is shown in Table 16. A ln - ln plot of the data shown in Figure 12 gives a straight line with a slope of -0.114 and with a standard deviation of +0.002. Therefore the water dependency in the rate equation is -0.11 or

$$\text{Rate} = k \frac{1}{[H_2O]_o^{0.11}} \tag{50}$$

These runs show that increasing the water concentration decreases the oxygen uptake. It is evident that rigorous care must be taken to exclude water in kinetic runs. A possible explanation for the decrease is that the water complexes with the cobalt and thereby reduces its efficiency. Pure tetralin under these same conditions shows no apparent oxygen uptake.

Effect of quinone concentration. A series of three runs was made at a constant cobalt concentration of 0.95 mM. The quinone concentration was varied from 0.50 to 1.50 mM. The effect on the rate of oxygen uptake is shown in Table 17. A ln - ln plot of the data shown in Figure 13 gives a good straight line with a slope of -0.306 and a standard deviation of +0.007.

The rate of the reaction is inversely proportional to the quinone concentration and its effect is greater than that of water. Hence quinone seems to be more effective than water in complexing with cobalt.

TABLE 16

EFFECT OF WATER ON COBALT SYSTEMS

(100 ml. tetralin, 70°, 1 atm. 0_2)

$[Co]_o$ x 10^5	$[H_20]_o$ x 10^3	ln $[H_20]_o$ + 6.91	Rate mm. 0_2/hr.	ln Rate
0.95	55.4	4.012	77	4.605
0.95	27.7	3.315	83	4.419
0.95	5.54	1.712	100	4.344
0.95	none		112	

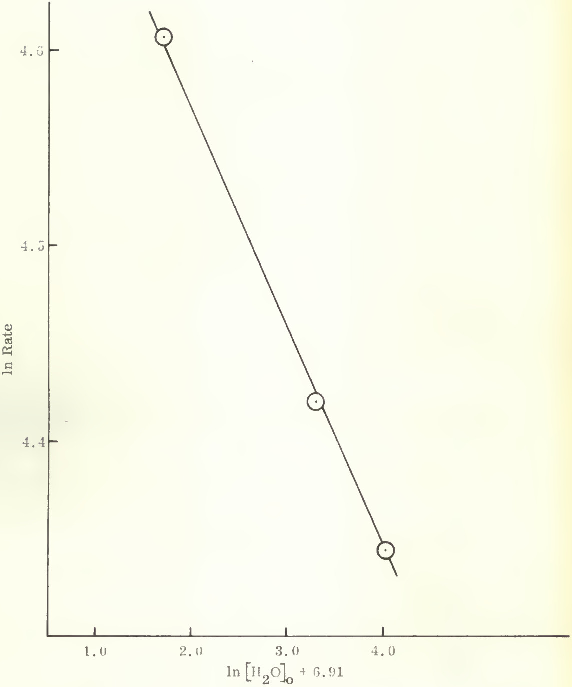


Figure 12. Plot of ln Rate versus $[H_2O]_o$ (100 ml. tetralin, 70°, 1 atm. O_2)

TABLE 17

EFFECT OF QUINONE ON COBALT SYSTEMS

(100 ml. tetralin, 0.95×10^{-5} M cobalt (II) naphthenate, 70°, 1 atm. O_2)

$[\text{Quinone}]_o$ $\times 10^3$	$\ln[\text{Quinone}]_o$ $+ 6.91$	Rate mm. O_2/hr.	ln Rate
none		112	
0.50	-0.693	70	4.249
1.00	0.000	57	4.043
1.50	0.405	51	3.912

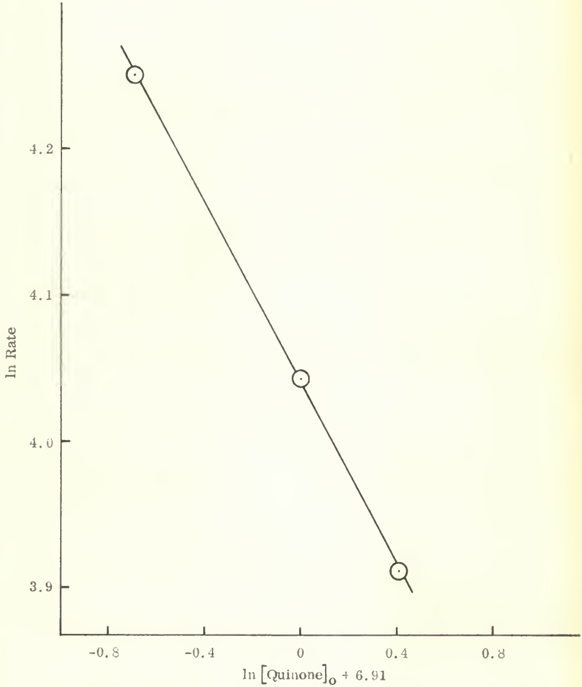


Figure 13. Plot of ln Rate versus ln $[\text{Quinone}]_o$ (100 ml. tetralin, 0.95 x 10^{-5} M cobalt (II) naphthenate, 70^o, 1 atm. O_2)

Effect of tetralin hydroperoxide concentration. Three runs were made with THP and cobalt to determine the effect on the rate of reaction. The results are presented in Table 18 and plotted in Figure 14.

In this series the rate of oxygen uptake decreases on addition of THP. A possible explanation for this observed effect will be presented in the Discussion section.

In an effort to investigate this system further, a series of sodium thiosulfate titrations were made to determine the THP concentration from the amount of iodine liberated from potassium iodide.

Three samples of the run containing 25 mM THP and 0.95×10^{-5} M cobalt were titrated at the end of the run (3.25 hours) and they were found to have a THP concentration of approximately 400 mM.

A large sample was centrifuged to determine if the THP had dropped out of solution and analysis showed that it had not. The concentration had increased to approximately 575 mM in THP which is reasonable since the oxidation process was not quenched.

A large amount of cobalt was then added to the sample so that the resultant cobalt concentration was 2.38 mM. The color of the sample turned green-brown and a white precipitate formed. Two samples of this mixture were then titrated. The first showed a THP concentration of 280 mM and the second (which was titrated about 5-10 minutes later) gave a concentration of 170 mM. This showed that the THP was decomposing.

The mixture was then centrifuged for one hour and titration showed that the concentration of the clear upper layer had fallen to a negligible

TABLE 18

EFFECT OF TETRALIN HYDROPEROXIDE ON COBALT SYSTEMS

(100 ml. tetralin, 70°, 1 atm. 0_2)

$[Co]_o$ x 10^5	$[THP]_o$ x 10^3	Rate mm. 0_2/hr.
1.19	none	130
1.19	1.00	115
0.95	none	112
0.95	5.00	109
0.95	25.0	87

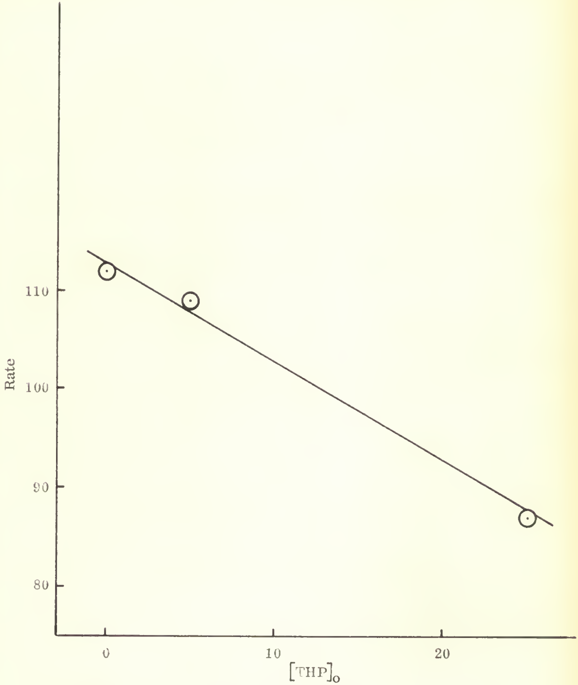


Figure 14. Plot of Rate versus $[\mathrm{THP}]_o$ (100 ml. tetralin, 70°, 1 atm. O_2)

amount. The precipitate from the lower layer contained no appreciable amount of THP. Unfortunately, this titration method is not sensitive enough to accurately detect concentrations below 5 mM. It seems likely that the cobalt is decomposing some of the THP but that the rate of THP formation is greater than its decomposition rate and thus the effect is masked.

In summary, the THP concentration increased during this run approximately 16 fold and remained in solution. On addition of a large amount of cobalt (2.38 mM) the concentration of THP slowly dropped to a negligible value. The rate of decomposition of THP is now evidently greater than the rate of formation.

In order to determine if the initial THP concentration affected the observed build-up of THP, a titration was made on a run containing the same initial cobalt concentration of 0.95 mM but no initial THP. The THP content was found to be approximately the same as in the above run containing both cobalt and THP initially.

Effect of 1,4-dimethoxybenzene concentration. This run was made to determine the effect of a disubstituted HQ (with no phenolic hydrogens) in a cobalt system. The cobalt concentration was 2.38×10^{-5} M and the 1,4-dimethoxybenzene concentration was 1:46 mM. The rate of oxygen uptake was 150 mm. in 30 minutes, or more than double that of the corresponding run containing only cobalt.

This run seems to indicate that the replacement of the phenolic hydrogens with methoxy groups causes the compound to act as an accelerator instead of an inhibitor.

Effect of dibutylcresol concentration. Two runs were made at concentrations of 2.38×10^{-5} M which is the same as in the previous series but greater than the concentration in the THP series. The DBC concentration in the first run was 2.00 mM and in the second it was 8.00 mM. The first run showed only a 5 mm. oxygen pressure decrease after 55 hours and the second had taken up 3 mm. of oxygen after 28 hours. Both runs showed very good protection at this cobalt concentration

Effect of p-methoxyphenol concentration. One run was made with the monosubstituted HQ, p-methoxyphenol, at a concentration of 1.25 mM. The cobalt concentration was 2.38×10^{-5} M and 2.00 mM of THP were added. The run was left on for 44 hours and only 25 mm. of oxygen were taken up. A corresponding run using HQ instead of p-methoxyphenol gave an induction period of 8.18 hours.

A titration was made after the run was over and showed no significant THP concentration change.

In summary, the series of runs with methoxy substituted hydroquinones shows that the absence of phenolic hydrogens in 1,4-dimethoxybenzene greatly accelerates the rate of oxygen uptake and the presence of one phenolic hydrogen in p-methoxyphenol appears to give better protection or inhibition than hydroquinone with its two phenolic hydrogens.

B. 2,2'-Azobisisobutyronitrile Systems

AIBN-no additives. One run was made at an AIBN concentration of 18.00 mM in 100 ml. of tetralin and one atmosphere oxygen pressure.

The rate of oxygen uptake for the first hour was 130 mm. This value was used as the standard with which to compare the following runs.

Effect of water on AIBN systems. The effect of water was studied by a run with an AIBN concentration of 18.00 m$\underline{M}$ and a water concentration of 55.4 m$\underline{M}$. The oxygen uptake in this system was 127 mm. This is equivalent, within experimental error, to the pressure decrease in the previous run which did not contain water.

In the cobalt system, the run with a water concentration of 55.4 m$\underline{M}$ showed a pressure drop of 77 mm. as compared to a pressure drop of 112 mm. in the absence of water. This indicates that the process that occurs in cobalt systems containing water which decreases the rate of oxygen absorption does not occur in AIBN systems.

Effect of quinone on AIBN systems. A run was made that contained 18.00 m$\underline{M}$ of AIBN and 1.50 m$\underline{M}$ of quinone. The rate of oxygen uptake for the first hour was 130 mm. which is the same rate as the run containing no quinone.

In the analogous runs in the cobalt series, the oxygen pressure decrease in the presence of 1.50 m$\underline{M}$ of quinone was 51 mm. and 112 mm. for the run containing only cobalt. Thus it appears that quinone is capable of interacting in cobalt systems but not in AIBN systems.

Effect of p-methoxyphenol on AIBN systems. A series of eight kinetic runs were made at 60°, 70° and 80° with both p-methoxyphenol and AIBN. The results are presented in Table 19.

TABLE 19

EFFECT OF p-METHOXYPHENOL CONCENTRATION ON INDUCTION PERIOD

(100 ml. tetralin, 70°, 1 atm. 0_2)

Temp.	$[\mathrm{AIBN}]_o$ x 10^3	[p-Methoxyphenol] x 10^3	t_i hours	Stoichio.
60	5.83	0.971	12.40	2.12
60	17.48	1.46	5.96	2.27
70	5.83	0.971	3.36	2.43
70	8.74	1.46	3.33	2.41
70	17.48	1.46	1.48	2.42
80	5.96	1.94	*	
80	5.96	2.91	*	
80	5.96	4.86	*	

*t_i not well defined for these runs.

The runs at 60° and 70° showed a slow oxygen uptake during the induction period which indicates that the inhibitor is not very efficient in capturing radicals. The runs at 80° did not show a well defined induction period but only a slow irregular oxygen uptake. Since this anomalous behavior is manifested at 80°, a plausible explanation is that additional radicals are generated by the termal decomposition of the substrate.

The values for the stoichiometry averaging 2.42 radicals per molecule at 70° (Table 19) show that p-methoxyphenol is a better inhibitor than HQ in AIBN systems. This is the same conclusion that was obtained in cobalt systems.

Effect of quinhydrone on AIBN systems. The effect of quinhydrone, a molecular compound of HQ and quinone, was studied by a run containing 4.35 m*M* AIBN and 2.40 m*M* quinhydrone. The induction period was 12.90 hours. The calculated stoichiometry is 1.6 radicals stopped per molecule of quinhydrone.

DISCUSSION

The results of this research will be discussed in this section on the basis of current free radical theory with particular attention devoted to consideration of the mechanism of inhibitor action and to the cobalt catalyzed decomposition of tetralin hydroperoxide. The section is divided into three parts. The first part discusses the inhibition process in non-branching initiator systems and the second discusses the inhibition process in branching catalyst systems. The last part is a discussion of the effects of additives in branching and non-branching systems.

I. The Inhibition Process in Non-Branching Initiator Systems

The experimental results in AIBN initiated autoxidation using tetralin as a substrate has verified four important ideas that parallel the work of Weinle (41) in which cumene was used as a substrate. They may be summarized as follows:

1. Inhibition is a result of reaction between free radicals produced in the system and the inhibitor.

2. The inhibition reaction is reproducible and can be correlated to the stoichiometry of the inhibitor.

3. The stoichiometry of the inhibitor can be determined by means of the radical counting technique and the initiator efficiency. For HQ this value is 1.1 radicals per molecule, for DBC it is 2.0 radicals per molecule, for quinhydrone it is 1.6 radicals per molecule and for p-methoxyphenol it is 2.4 radicals per molecule at 70°.

4. At high temperatures and during long induction periods the inhibitor is destroyed by radicals or processes other than those derived from the decomposition of AIBN.

The present work plus Weinle's (41) contribution establish that the principal processes occurring during the induction period in AIBN systems are well characterized and predictable over a much wider range of conditions than has previously been reported. This predictability may be expressed quantitatively by the following kinetic equation, derived by Weinle, in accordance with the principles employed in explaining the results:

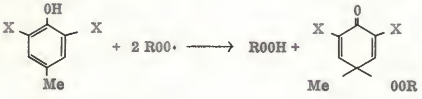
$$t_i = \frac{1}{k_i} \left[\ln 2 \, [\text{AIBN}]_0 - \ln (2 \, \alpha \, [\text{AIBN}]_0 - S \, [A]_0) \right] \qquad (51)$$

where t_i is the length of induction period, k_i is the specific rate constant for AIBN decomposition, α is the initiator efficiency, S is the inhibitor stoichiometry and $[A]_0$ equals initial concentration of inhibitor.

A test of equation 51 is shown in Figures 15 and 16. The data for these plots are from Tables 4 and 7 which show the effect of HQ and DBC, respectively, on the induction period at 70°. A straight line with a slope equal to $1/k_i$ will be obtained if equation 51 is valid. The calculated value of $1/k_i$ is 1.7×10^4 seconds (17). The values obtained from the least square slope are 2.6×10^4 seconds for the HQ series and 0.98×10^4 seconds for the DBC series.

Since the characterization and predictability of the principal processes occurring during the induction period in tetralin have been established, the results of the inhibitor stoichiometry measurements may be used to deduce possible mechanisms for the destruction of the inhibitor.

For DBC the mechanism involves the following process:



I

(52)

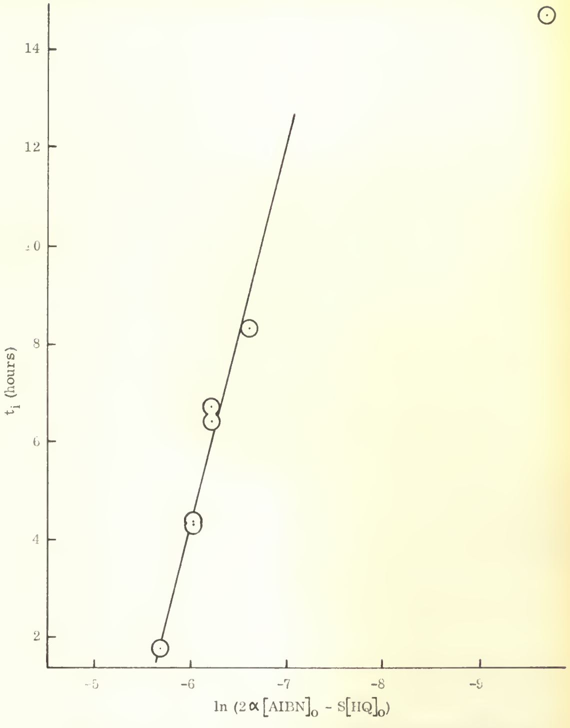


Figure 15. Plot of t_i versus ln (2α[AIBN]$_o$ - S[HQ]$_o$) (Data from Table 6)

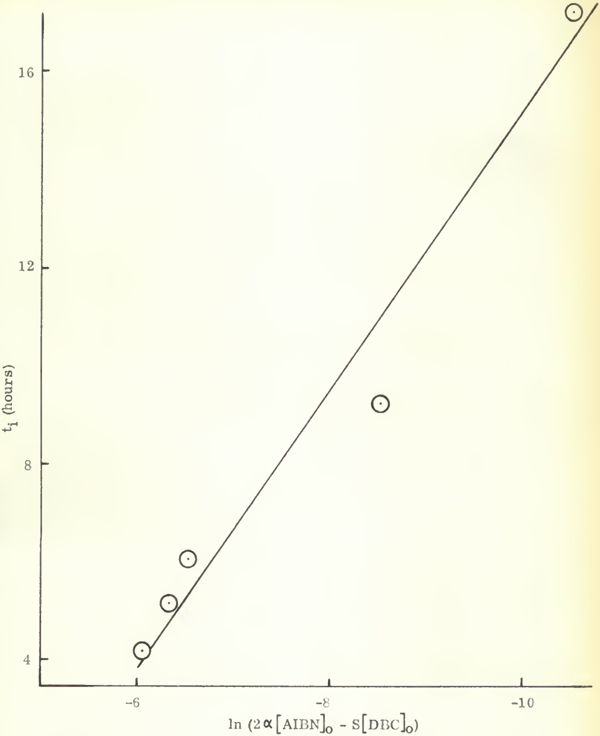
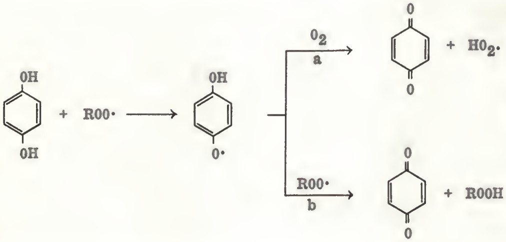


Figure 16. Plot of t_i versus ln $(2\alpha[AIBN]_o - S[DBC]_o)$ (Data from Table 9)

where X represents the t-butyl group.

Justification for this assignment comes from the observation of a radical stoichiometry of 2.0 (7, 65), isolation of the quinoid type product I from systems of DBC and radical initiators (42, 43) and from the kinetics of DBC systems containing cobalt (II) naphthenate to be discussed in Part II of this section.

The mechanism of HQ and similar inhibitors is still not clear. However, considerable evidence is accumulating for the following scheme:



(53)

Evidence for this mechanism may be summarized as follows:

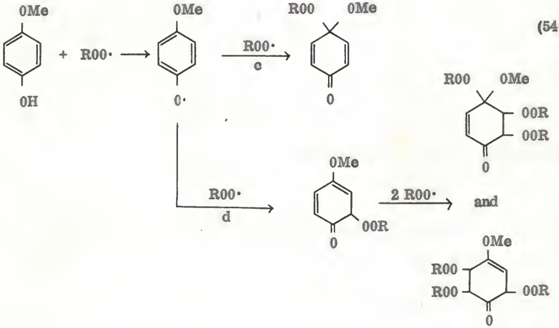
1. Quinones have been detected in solutions inhibited by hydroquinones (50, 51, 66-69).

2. The observed stoichiometry of HQ in both tetralin and cumene (41) is about 1.1 radicals per molecule. This stoichiometry is possible if the rate of step b is 1.2 times that of step a, which means that the semiquinone radical must react quite rapidly with oxygen. This has been shown to occur by Weissberger et al. (66, 70).

3. If step a is important, the induction period in hydroquinone systems should be increased at lower oxygen pressures. This has been observed by Lloyd (2).

4. Quinhydrone might be expected to have a higher stoichiometry than hydroquinone on the basis of the above mechanism. This is because the semiquinone, complexed with quinone, would not react as readily with oxygen but would be available to react with the more reactive tetralylperoxy radical. The observed stoichiometry of quinhydrone is 1.6 radicals per molecule which is considerably greater than the stoichiometry of HQ.

5. The observed stoichiometry of p-methoxyphenol of 2.4 radicals per molecule can be accounted for in terms of a modification of the above mechanistic scheme. In this case the reactions would become:



(54)

The rate of step c would have to be four times that of step d. This is reasonable since the one position has a higher electron density.

6. The observed stoichiometry of several other hydroquinone type inhibitors is consistent with the mechanism presented. 2, 5-Di-t-butyl hydroquinone has been reported (7) to have a stoichiometry of 0.85 radicals per molecule which suggests that the oxidation of the semiquinone is more important in this case than in hydroquinone. Since this semiquinone is sterically hindered it is reasonable to expect that oxygen might attack more readily than the bulky tetralylperoxy radical.

In summary, the portion of this work involving the AIBN initiator has shown clearly that the principal processes occurring during the induction period are well characterized and predictable over a wide range of conditions. In addition, it has provided inhibitor stoichiometries which have been used in conjunction with other information to postulate mechanisms for the inhibitors used in this study.

II. The Inhibition Process in Branching Catalyst Systems

Kinetic studies of the autoxidation of tetralin in the presence of cobalt (II) naphthenate were investigated in order to compare the inhibition process in branching and non-branching systems. If the mechanism of inhibition involves hydrogen abstraction by the peroxy radical, a hydroperoxide will be formed. Cobalt ions are known to decompose hydroperoxides to give radicals. Therefore, an inhibitor that functions by hydrogen abstraction should give poor protection in cobalt systems.

A. Kinetics of dibutylcresol-cobalt-tetralin hydroperoxide systems

The proposed mechanism for DBC destruction was given in Part I of this section. Weinle (41) has derived an equation for the kinetics of the induction period process assuming the proposed mechanism to be operative. He found excellent correlation between the equation and the experimental results. Weinle's equation is:

$$t_i = \frac{1}{k_b [\mathrm{Co}]^x} \left[\ln [\mathrm{THP}]_o - \ln ([\mathrm{THP}]_o - [\mathrm{DBC}]_o) \right] \tag{55}$$

where t_i is the length of induction period, k_b is the specific rate constant for cobalt catalyzed decomposition of THP and x is the number of cobalt ions involved in the decomposition.

Since Weinle found excellent correlation between the equation and experiments on all parameters in the equation in cumene systems, it was decided to test the equation on only one parameter in the tetralin system. The parameter chosen was the DBC concentration and a plot of t_i versus ln $([THP]_0 - [DBC]_0)$ from the data of Table 13 is given in Figure 9. The points describe a straight line with a slope of -5.05 and a standard deviation of ±0.56 which strongly suggests that the mechanism of DBC is the same in tetralin and cumene.

This correlation also indicates that the peroxide decay process is similar in the two substrates. From the slope of the line in Figure 9 the specific rate constant for the cobalt catalyzed decomposition of THP may be calculated and the value compared with the corresponding value in cumene. These values are:

$$k_b = 9.6 \times 10^4 \text{ liters/mole/second in tetralin}$$

$$k_b = 4.5 \times 10^5 \text{ liters/mole/second in cumene}$$

It thus appears that the specific rate constant for the cobalt catalyzed THP decomposition is approximately one-fifth that of the corresponding cumene hydroperoxide decomposition.

B. Kinetics of hydroquinone-cobalt-tetralin hydroperoxide systems

Perhaps the most striking difference between HQ and DBC in the cobalt systems is the fact that HQ is a much better inhibitor than is DBC. Since the kinetics of the process in DBC-cobalt-THP systems has been characterized and the rate constants have been determined, the only reasonable explanation for the greater efficiency of HQ in protecting cobalt systems is that somehow HQ, or its product quinone, complexes with the cobalt catalyst. This could slow down the radical producing peroxide decay process.

To investigate this possibility quantitatively, quinone was added to uninhibited tetralin containing cobalt and THP. The rate of oxygen uptake dropped sharply. In contrast, no change in the rate of oxygen uptake was observed when the same amount of quinone was added to uninhibited tetralin containing AIBN. In another experiment quinone was added to a system containing HQ, cobalt and hydroperoxide. This resulted in a large increase in induction period compared to the same system without quinone.

It is possible to derive an equation for the rate processes occurring during the induction period taking into account complexing of the cobalt catalyst with quinone. This equation, derived in the Appendix, is:

$$t_i = \frac{[HQ]_o^z \, K^x}{z \, k_b \, [Co]_o^x \, [R00H]_o} \qquad (85)$$

where t_i is the length of induction period, K is the equilibrium constant for the quinone-cobalt complexing process, k_b is the specific rate constant for the THP decay process, x is the number of cobalt ions involved in the decomposition of THP and z equals xy + 1 where y is the number of quinone molecules involved in cobalt complexing. However, x and y may have a broader significance which will be explained later.

Before testing this equation with the experimental data, it might be well to examine the implications of this equation. The value (or values) of the equilibrium constant (K) is likely to be the product of two or more equilibrium constants for individual steps in the complexing process. Thus each of the processes:

$$\begin{aligned} Co + Q &\rightleftharpoons CoQ \qquad K_a \\ CoQ + Q &\rightleftharpoons CoQ_2 \qquad K_b \\ CoQ_2 + Q &\rightleftharpoons CoQ_3 \qquad K_c \end{aligned} \tag{56}$$

where Q is quinone, may be represented by an equilibrium constant. The equilibrium constant for the overall process will be the product of the equilibrium constants for each step or

$$K_{overall} = K_a K_b K_c \tag{57}$$

In equation 85, K may have different values depending on the ratio of cobalt to quinone in the system. In systems containing a small ratio of cobalt to quinone, K may be the product of K_a, K_b and K_c whereas in systems with a higher cobalt to quinone ratio K may be the product of K_a and K_b. Changes in the value of K can occur in series of runs in which HQ or quinone concentrations are varied. It can be shown that the effect of such a change in complexing will change the values of the exponents for $[HQ]_o$ and $[Co]_o$ in equation 85.

Turning to the data on the HQ-cobalt-THP systems, the correlations between experimental results and equation 85 can now be made. The equation predicts the following relationships between t_1 and each of the experimental parameters

$$t_1 = \frac{k}{[THP]_o} \qquad t_1 = \frac{k}{[Co]_o^x} \qquad t_1 = k\,[HQ]_o^z \tag{58}$$

Each of these relationships has been observed in tetralin systems containing HQ. The first and second were observed by Lloyd (2) and his data are reproduced in graph form in Figures 17 and 18. The value of x from Lloyd's work is 3. Two series of data on HQ dependency were reported in Tables 10 and 11 and plotted in Figures 6 and 7. Both conform well to the relation $t_i = k\ [HQ]_o^3$. It thus appears that in tetralin systems over the concentration ranges reported in this work and in that of Lloyd, equation 85 takes the form

$$t_i = \frac{K^3\ [HQ]_o^3}{3\ k_b\ [Co]_o^3 [THP]_o} \tag{59}$$

This suggests that only one molecule of quinone is complexed with the cobalt ion in the principal equilibrium process. The value of K then becomes 1.2 x 10^1. It is interesting to note here that Weinle (41) found that in cumene systems equation 85 takes the form

$$t_i = \frac{K^6 [HQ]_o^7}{7\ k_b\ [Co]_o^6\ [CHP]_o} \tag{60}$$

where $[CHP]_o$ is the initial concentration of cumene hydroperoxide. In this case apparently three molecules of quinone are complexed with the cobalt. The high value for the exponent for cobalt suggests that the complexing equilibria are more complex in cumene than in tetralin.

In summary, it has been shown both qualitatively and quantitatively that the increased efficiency of HQ as an inhibitor in branching systems is due to the complexing of quinone with cobalt thereby reducing the effectiveness of cobalt as a catalyst for radical production.

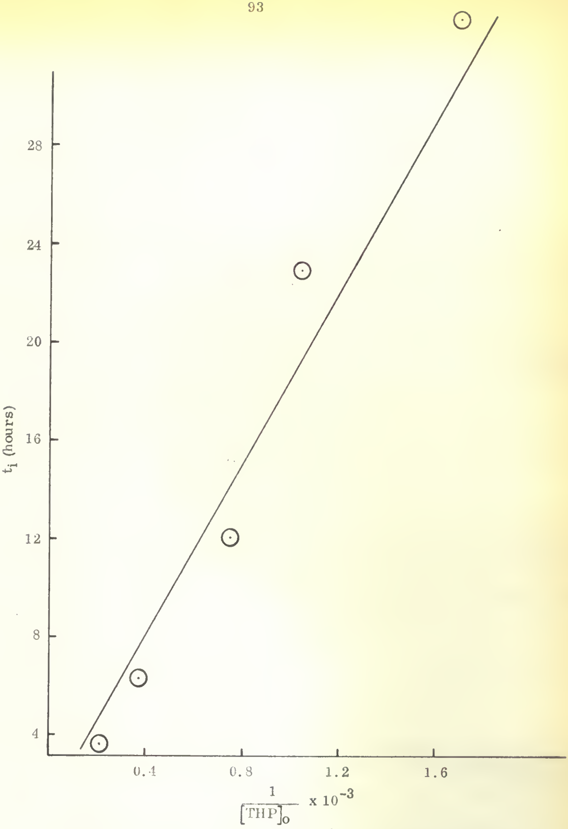


Figure 17. Plot of t_i versus $1/[THP]_o$ (100 ml. tetralin, 2.00 m$\underline{M}$ HQ, 2.50×10^{-5} $\underline{M}$ cobalt (II) naphthenate, 70°, 1 atm. O_2)

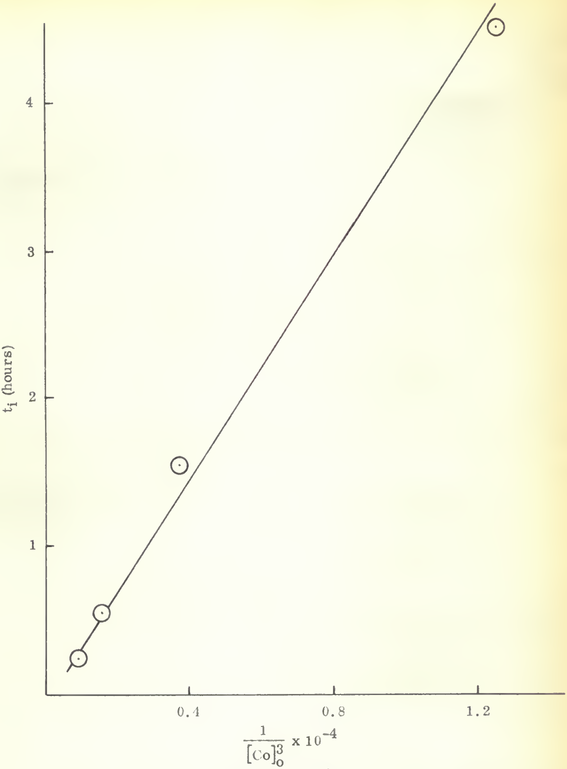


Figure 18. Plot of t_i versus $1/[\mathrm{Co}]_o^3 \times 10^{-4}$ (100 ml. tetralin, 1.25 m$\underline{M}$ HQ 70°, 1 atm. O_2)

III. Kinetics of Cobalt (II) Naphthenate Catalyzed Autoxidation of Tetralin

The results of the studies using the cobalt catalyst in the absence of phenolic inhibitors have shown that the empirically derived rate law for this process, under the experimental conditions employed in this work, is:

$$\frac{-d\left[O_2\right]}{dt} = \frac{k_1 \left[Co\right]_o^{0.6}}{1 + k_2\left[Q\right]_o^{0.3} + k_3\left[H_2O\right]_o^{0.11}} - k_4\left[Co\right]_o^{x}\left[THP\right]_o \qquad (61)$$

where $[Co]_o$, $[Q]_o$, $[H_2O]_o$ and $[THP]_o$ represent the initial concentrations of cobalt, quinone, water and THP respectively and k_1, k_2, k_3 and k_4 are rate constants. This equation illustrates that the rate of oxygen uptake is catalyzed by the cobalt species but that this catalysis is inhibited somewhat by quinone, water or THP. In addition, the rate law indicates that the inhibition by THP is different in nature than the inhibition by quinone and water.

The catalysis by cobalt is well known and expected although the mechanism of the process is still very much in doubt. If the catalysis involves radical initiation by cobalt ions and a bimolecular termination step, the rate law should indicate a 0.5 order dependency of the rate on the cobalt concentration. The observed 0.6 order dependency is in good agreement with this and with the reaction scheme:

$$\begin{aligned} &(0_2,\ \mathrm{R00H},\ ?) + \mathrm{Co}^{++} \longrightarrow \mathrm{R00}\cdot \\ &\mathrm{R00}\cdot + \mathrm{RH} \longrightarrow \mathrm{R00H} + \mathrm{R}\cdot \\ &\mathrm{R}\cdot + 0_2 \longrightarrow \mathrm{R00}\cdot \\ &2\ \mathrm{R00}\cdot \longrightarrow \text{inert products} \end{aligned} \qquad (62)$$

The nature of the first step in the scheme is unknown. It has been suggested (10) that the cobalt may react with oxygen to produce a cobalt peroxy radical which might initiate chains as follows:

$$\mathrm{Co}^{++} + 0_2 \longrightarrow \mathrm{Co}^{++}0_2\cdot \qquad (63)$$

It is known that cobalt produces radicals by decomposition of hydroperoxides (12, 43, 52). However, the cobalt catalysis also occurs in systems containing no detectable concentration of hydroperoxides. Moreover, at the cobalt concentrations used in this work, addition of hydroperoxide inhibits rather than accelerates the reaction.. The most reasonable interpretation of this data is that cobalt initiates radicals by reacting according to process 63.

Quinone and water have been observed to inhibit tetralin autoxidation. This would occur if the quinone and water complexed with cobalt so as to prevent the cobalt from initiating radicals. This is similar to the inhibition observed for the hydroquinone-THP-cobalt systems discussed in the previous section.

The nature of this phenomenon can be visualized mathematically as follows:

$$\frac{-d[0_2]}{dt} = k\,[\mathrm{Co}]^{0.6} \qquad (64)$$

which is the observed rate law for cobalt catalysis in the absence of water and quinone. If the following equilibrium is set up on addition of water or quinone (Q):

$$\mathrm{Co} + x\mathrm{Q} \longrightarrow \mathrm{CoQ}x \tag{65}$$

then the active cobalt concentration will become:

$$[\mathrm{Co}] = \frac{[\mathrm{Co}]_o}{1 + K[\mathrm{Q}]_o^x} \tag{66}$$

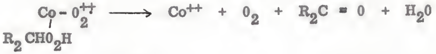
where Co_o and Q_o are the initial concentrations of cobalt and quinone, K is the equilibrium constant for the complexing reactions and x is the number of quinone molecules involved in the complex.

Substituting equation 66 into equation 64 gives:

$$\frac{-d[\mathrm{O}_2]}{dt} = \frac{k\,[\mathrm{Co}]_o^{0.6}}{(1 + K[\mathrm{Q}]_o^x)^{0.6}} \simeq \frac{k\,[\mathrm{Co}]_o^{0.6}}{1 + 0.6K[\mathrm{Q}]_o^x} \tag{67}$$

If the above assumptions are valid, the constants k_2 and k_3 in equation 61 become 0.6 times the equilibrium constant for the quinone and the water complexing processes respectively.

Equation 61, as noted above, indicates that the inhibition by THP is of a different nature than that shown by quinone and water. The form of the equation suggests that THP is involved in a reaction with cobalt which is competitive with the process in which cobalt produces radicals. A reasonable competition process is that if oxygen and THP are complexed with cobalt at the same time, a reaction of the type



$$\underset{R_2CH0_2H}{Co} - 0_2^{++} \longrightarrow Co^{++} + 0_2 + R_2C = 0 + H_20 \qquad (68)$$

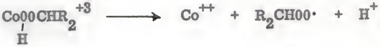
might occur. This could be represented stepwise as:

$$Co^{++} + R_2CH00H \longrightarrow Co^{+++} + R_2CH0\cdot + 0H^- \qquad (69)$$

$$R_2CH0\cdot + Co0_2^{+++} \longrightarrow R_2C = 0 + Co0_2{}^{+++} \qquad (70)$$

$$Co0_2H^{+++} \longrightarrow Co^{++} + 0_2 + H^+ \qquad (71)$$

The reaction, analogous to equation 71, of the cobalt decomposition of hydroperoxide to form radicals could occur as follows:



$$Co\underset{H}{0}0CHR_2{}^{+3} \longrightarrow Co^{++} + R_2CH00\cdot + H^+ \qquad (72)$$

In summary, the results of this section have been interpreted so as to formulate the radical initiation process as involving reaction of oxygen with cobalt to give the radical initiator. This initiator may be prevented from forming if the cobalt complexes with either quinone or water. The initiator may also enter into a reaction with THP. This latter reaction reduces the rate of radical initiation by a competitive reaction which regenerates the cobalt. The cobalt is then free to react with oxygen to produce the initiator. The initiator may then initiate chains or react with THP. In this competitive process, all of the cobalt is free to react. In the water and the quinone complexing process, much of the cobalt is unable to react.

At higher concentrations of THP, reaction of cobalt with oxygen is probably eliminated because the cobalt is complexed with THP. Under these conditions radical initiation occurs entirely by decomposition of the hydroperoxide. This latter phenoma has been observed by many workers (12, 30, 35).

SUMMARY

Studies of the inhibition process in non-branching systems have established that the reactions between free radicals and inhibitors are well characterized and predictable and can be related to the stoichiometry of the inhibitor. The stoichiometries of the inhibitors hydroquinone, p-methoxyphenol and quinhydrone have been found to be 1.1, 2.4 and 1.6 radicals per molecule at 70°. The radical producing efficiencies of 2,2'-azobisisobutyronitrile in tetralin substrate have been determined at 60°, 70° and 80° and are 0.50, 0.54 and 0.56 respectively. Mechanisms are proposed for the inhibition reactions of the above inhibitors and shown to be consistent with a substituted hydroquinone whose stoichiometry has been reported by other workers.

The results of studies in branching catalyst systems provided evidence that the mechanism of dibutylcresol is the same in tetralin as it is in cumene by showing that Weinle's (41) equation is obeyed for dibutylcresol in tetralin. It was shown qualitatively and quantitatively that the behavior of hydroquinone in cobalt systems is due to formation of a complex between cobalt and quinone. This complex prevents cobalt from decomposing hydroperoxides. An equation was developed to quantitatively express the complexing process. This equation

$$t_1 = \frac{[HQ]_o^z \; K^x}{z\, k_b\, [Co]_o^x [ROOH]_o} \qquad (85)$$

gave good correlation with the experimental results.

The results of the final section have shown that the rate of uninhibited oxidation is proportional to $[Co]^{0.6}$. The addition of water, quinone or tetralin hydroperoxide was found to decrease the rate of oxygen uptake. The empirically observed rate law for the above observations is

$$\frac{-d[O_2]}{dt} = \frac{k_1 [Co]_o^{0.6}}{1 + k_2 [Q]_o^{0.3} + k_3 [H_2O]_o^{0.11}} - k_4 [Co]_o^{x} [THP]_o \qquad (61)$$

This indicates that the inhibition by quinone and water is of a different nature than that of tetralin hydroperoxide. An explanation for the two types of inhibition has been presented in terms of

1. Complexing of water and quinone with cobalt to reduce its catalytic activity.

2. A competing reaction of tetralin hydroperoxide with the initiator $CoO_2^{++\cdot}$ to reduce the initiating efficiency of the radical.

BIBLIOGRAPHY

1. H. L. J. Bäckström, J. Am. Chem. Soc., 49, 1460 (1927).

2. W. G. Lloyd, "Autoxidation Inhibition of Tetralin: A Study by Induction Period Analysis," Doctoral Dissertation, Michigan State University, 1957.

3. C. Walling, "Free Radicals in Solution," John Wiley and Sons, New York, 1957, Chapters 9-11.

4. C. E. Frank, Chem. Revs., 46, 155 (1950).

5. G. A. Russell, J. Chem. Ed., 36, 111 (1959).

6. L. Bateman, Quart. Rev. 8, 147 (1954).

7. C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. Sen, J. Am. Chem. Soc., 77, 3233 (1955).

8. Discussions Faraday Soc., 2 (1947); Trans. Faraday Soc., 42, 99-398 (1946).

9. L. Bateman, Quart. Revs., 8, 147 (1954).

10. N. Uri, Nature, 177, 1177 (1956).

11. A. Robertson and W. A. Waters, J. Chem. Soc., 1574 (1948).

12. A. R. Woodward and R. B. Mesrobian, J. Am. Chem. Soc., 75, 6189 (1953).

13. H. S. Blanchard, J. Am. Chem. Soc., 82, 2014 (1960).

14. G. S. Hammond, J. N. Sen and C. E. Boozer, J. Am. Chem. Soc., 77, 3244 (1955).

15. D. Verdin, Trans. Faraday Soc., 57, 484 (1961).

16. C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, J. Am. Chem. Soc., 71, 2661 (1949).

17. J. P. Van Hook and A. V. Tobolsky, *Ibid.*, *80*, 779 (1958).

18. F. M. Lewis and M. S. Matheson, *Ibid.*, *71*, 747 (1949).

19. C. F. H. Tipper, *Quart. Revs.*, *11*, 313 (1957).

20. G. S. Hammond, C.-H. S. Wu, O. D. Trapp, J. Warkentin and R. T. Keys, *J. Am. Chem. Soc.*, *82*, 5394 (1960).

21. M. Talat-Erben and S. Bywater, *Ibid.*, *77*, 3710, 3712 (1955).

22. C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc. (London)*, *A 198*, 252 (1949).

23. G. A. Russell, *J. Chem. Ed.*, *36*, 111 (1959).

24. E. H. Farmer and H. Sundralingham, *J. Chem. Soc.*, 121 (1942).

25. K. I. Ivanov, V. K. Savinova and E. G. Mikhailova, *Compt. rend. acad. sci. U.R.S.S.*, *25*, 34 (1939); *Chem. Abs.*, *34*, 3973_9 (1940).

26. M. Hartman and M. Seiberth, *Helv. Chem. Acta.*, *15*, 1390 (1932).

27. R. Johnson, U. S. Patent 2,568,639 (1951); *Chem. Abs.*, *46*, 5089_d (1952).

28. E. R. Bell, J. H. Raley, F. F. Rust, F. H. Senbold, Jr. and W. E. Vaughan, *Discussions Faraday Soc.*, *10*, 246 (1953).

29. P. George, E. H. Rideal and A. Robertson, *Proc. Roy. Soc. (London)*, *A 185*, 288 (1946).

30. A. Robertson and W. A. Waters, *Trans. Faraday Soc.*, *42*, 201 (1946).

31. T. Yamada, *Researches Electrotech. Lab. (Tokyo)*, *411*, 1 (1937).

32. S. S. Medvedev, *Acta Physicochimica U.R.S.S.*, *9*, 395 (1938).

33. A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1578 (1948).

34. G. A. Russell, *J. Am. Chem. Soc.*, *79*, 3871 (1957).

35. H. S. Blanchard, *Ibid.*, *81*, 4548 (1959).

36. A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1585 (1948).

37. L. Bateman and A. L. Morris, *Trans. Faraday Soc.*, *49*, 1026 (1953).

38. C. E. H. Bawn, *J. Oil Colour Chem. Assoc.*, *36*, 443 (1953).

39. C. F. Cullis, *Bull. Soc. Chem. France* [5], *17*, 863 (1950).

40. H. A. Mattill, *J. Biol. Chem.*, *90*, 141 (1931).

41. P. L. Weinle, "Autoxidation Inhibition in Cumene," Doctoral Dissertation, University of Florida, 1961.

42. T. W. Campbell and C. M. Coppinger, *J. Am. Chem. Soc.*, *74*, 1469 (1952).

43. A. F. Bickell and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).

44. G. S. Hammond and U. S. Nandi, *J. Am. Chem. Soc.*, *83*, 1217 (1961).

45. G. S. Hammond, C. E. Boozer, C. E. Hamilton and J. N. Sen, *J. Am. Chem. Soc.*, *77*, 3238 (1955).

46. C. E. Boozer and G. S. Hammond, *Ibid.*, *76*, 3861 (1954).

47. C. E. Boozer, G. S. Hammond, C. E. Hamilton and C. Peterson, *Ibid.*, *77*, 3380 (1955).

48. C. Walling and M. G. Mayahi, *Ibid.*, *81*, 1485 (1959).

49. G. A. Russell, *J. Org. Chem.*, *24*, 300 (1959).

50. J. L. Bolland and P. ten Have, *Trans. Faraday Soc.*, *43*, 201 (1947).

51. M. S. Kharasch, E. Kawahara and W. Nudenberg, *J. Org. Chem.*, *19*, 1977 (1954).

52. C. E. H. Bawn, *Faraday Soc. Disc.*, *14*, 181 (1953).

53. E. Dyer, K. R. Carle and D. E. Weiman, *J. Org. Chem.*, *23*, 1464 (1958).

54. W. S. Emerson, J. W. Heyd, V. E. Lucas, W. B. Cook, W. I. Lyness and J. K. Stevenson, *J. Am. Chem. Soc.*, *70*, 3764 (1948).

55. C. E. H. Bawn and J. E. Jolley, *Proc. Roy. Soc.* (*London*), *A 237*, 297 (1956).

56. F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Pittsburg, 1953, p. 79.

57. A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience, New York, 1954, pp. 96 ff.

58. G. J. Minkoff, Proc. Roy. Soc. (London), A 224, 176 (1954).

59. C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, J. Am. Chem. Soc., 71, 2661 (1949).

60. C. D. Hodgman (ed.), "Handbook of Chemistry and Physics," 42 ed., Chemical Rubber Publishing Co., Cleveland, 1960, pp. 764 ff.

61. W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, New York, 1951.

62. L. M. Arnett and J. H. Peterson, J. Am. Chem. Soc., 80, 779 (1958).

63. J. C. Bevington, J. H. Bradbury and G. M. Burnett, J. Polymer Sci., 12, 469 (1954).

64. J. C. Bevington, Trans. Faraday Soc., 51, 1392 (1955).

65. T. W. Campbell and G. M. Coppinger, J. Am. Chem. Soc., 74, 1469 (1952).

66. T. H. James and A. Weissberger, Ibid., 60, 98 (1938).

67. J. Pinnow, Z. wiss. Phot., 11, 289 (1913).

68. H. V. Euler and E. Brunius, Z. physik. Chem., 139, 615 (1928).

69. E. Lehmann and E. Tausch, Phot. Korr., 71, 17 (1935).

70. J. E. Levalle and A. Weissberger, J. Am. Chem. Soc., 69, 1821 (1947).

APPENDIX

APPENDIX

Derivation of an Equation for the Kinetics of the Induction Period Process in Hydroquinone-Cobalt-Hydroperoxide Systems

This derivation is based on the following assumptions.

1. Quinone complexes with the cobalt catalyst and this complex is unable to act as a catalyst.

2. An equilibrium or equilibria exists between complexed and active cobalt ions.

3. HQ reacts rapidly with all the radicals produced in the system to give quinone and hydroperoxide molecules.

4. Decomposition of the hydroperoxide is the source of all radicals.

Under these conditions, the rate of radical production equals $k_b [Co]^x [R00H]_o$ where k_b is the specific rate constant for the cobalt catalyzed hydroperoxide decomposition, $[Co]$ is the concentration of active cobalt, x is the number of cobalt ions involved in the decomposition step and $[R00H]_o$ is the initial concentration of hydroperoxide. According to the above assumptions, $[R00H]_o$ will remain constant as long as HQ is present.

The rate of inhibitor consumption parallels the rate of radical production or

$$\frac{-d\left[HQ\right]}{dt} = \text{Rate of radical production} = k_b \left[Co\right]^x \left[ROOH\right]_o \qquad (73)$$

If the cobalt is complexed by the quinone (Q):

$$Co + yQ \rightleftharpoons CoQy \qquad (74)$$

this may be represented by the equilibrium constant expression:

$$K = \frac{\left[CoQy\right]}{\left[Co\right]\left[Q\right]^y} \qquad (75)$$

which rearranges to:

$$\left[Co\right] = \frac{\left[CoQy\right]}{K\left[Q\right]^y} \qquad (76)$$

If K is large:

$$\left[CoQy\right] \simeq \left[Co\right]_o \qquad (77)$$

where $\left[Co\right]_o$ is the initial concentration of cobalt.

Rewriting equation 76 gives:

$$\left[Co\right] = \frac{\left[Co\right]_o}{K\left[Q\right]^y} \qquad (78)$$

The concentration of quinone at time t (Q_t) will be:

$$\left[Q\right]_t = \left[HQ\right]_o - \left[HQ\right]_t \qquad (79)$$

Substituting this into equation 78 yields:

$$\left[Co\right] = \frac{\left[Co\right]_o}{K\left(\left[HQ\right]_o - \left[HQ\right]_t\right)^y} \qquad (80)$$

Equation 80 can now be substituted in equation 73 to give:

$$\frac{-d\,[HQ]}{dt} = \frac{k_b\ [Co]_o^x\ [R00H]_o}{K^x\,([HQ]_o - [HQ]_t)^{yx}} \tag{81}$$

Rearranging and integrating between the limits t = 0 and t = t_i and the limits $[HQ] = [HQ]_o$ and $[HQ] = [HQ]_t$ where $[HQ]_o$ is the initial concentration of HQ and $[HQ]_t$ is the concentration of HQ at the end of the induction period. $[HQ]_t$ can be assumed to be equal to zero.

$$\int_{[HQ]_o}^{0} ([HQ]_o - [HQ]_t)^{yx}\, d\,[HQ] = \frac{-k_b\ [Co]_o^x\ [R00H]_o}{K^x} \int_0^{t_i} dt \tag{82}$$

$$\frac{[HQ]_o^{yx+1}}{yx + 1} = \frac{k_b\ [Co]_o^x\ [R00H]_o\ t_i}{K^x} \tag{83}$$

or

$$t_i = \frac{[HQ]_o^{yx+1}\ K^x}{(yx + 1)\ k_b\ [Co]_o^x\ [R00H]_o} \tag{84}$$

Setting yx + 1 equal to z gives

$$t_i = \frac{[HQ]_o^z\ K^x}{z\ k_b\ [Co]_o^x\ [R00H]_o} \tag{85}$$

BIOGRAPHICAL SKETCH

Nicholas Michaels was born July 21, 1935 at New York, New York. In June, 1952, he was graduated from De Witt Clinton High School. In June, 1956, he received the degree of Bachelor of Science from Iona College. In September, 1956, he enrolled in the Graduate School of Pennsylvania State University where he held a research assistantship in the Petroleum Refining Laboratory. In September, 1957, he enrolled in the Graduate School of the University of Florida and until the present time he has pursued his work toward the degree Doctor of Philosophy. At the University of Florida he held positions in the Department of Chemistry as a graduate assistant and teaching assistant.

Nicholas Michaels is married to the former Linda Susann Lee of Delray Beach, Florida. He is a member of Gamma Sigma Epsilon and Alpha Chi Sigma.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June 5, 1961

A H Gropp

Dean, College of Arts and Sciences

Dean, Graduate School

Supervisory Committee:

W. T. Lippincott

Chairman

G. B. Butler

C. E. Reid

R. C. Stoufer for H. H. Sisler

W H Beisler